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The Deleterious Chemical Effects of Concentrated Deicing Solutions on Portland Cement Concrete

Study SD2002-01
Literature Review

Prepared by
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16. Abstract

This research project investigated the effects of concentrated brines of magnesium chloride, calcium chloride, sodium chloride, and calcium magnesium acetate on portland cement concrete. Although known to be effective at deicing and anti-icing, the deleterious effects these chemicals may have on concrete have not been well documented. As a result of this research, it was determined that there is significant evidence that magnesium chloride and calcium chloride chemically interact with hardened portland cement paste in concrete resulting in expansive cracking, increased permeability, and a significant loss in compressive strength. Although the same effects were not seen with sodium chloride brines, it was shown that sodium chloride brines have the highest rate of ingress into hardened concrete. This latter fact is significant with respect to corrosion of embedded steel. The mechanism for attack of hardened cement paste varies with deicer chemical but in general, a chemical reaction between chlorides and cement hydration products results in the dissolution of the hardened cement paste and formation of oxychloride phases, which are expansive. The chemical attack of the hardened cement paste is significantly reduced if supplementary cementitious materials are included in the concrete mixture. Both coal fly ash and ground granulated blast furnace slag were found to be effective at mitigating the chemical attack caused by the deicers tested. In the tests performed, ground granulated blast furnace slag performed better as a mitigation strategy as compared to coal fly ash. Additionally, siloxane and silane sealants were effective at slowing the ingress of deicing chemicals into the concrete and thereby reducing the observed distress. In general, the siloxane sealant appeared to be more effective than the silane, but both were effective and should be considered as a maintenance strategy.

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Table of Acronyms

Acronym	Definition
AASHTO	American Association of State Highway and Transportation Officials
ACI	American Concrete Institute
ACR	Alkali Carbonate Reaction
ASR	Alkali Silica Reaction
ASTM	American Society for Testing and Materials
AVA	Air Void Analyzer
C_2S	Dicalcium Silicate
C_3A	Tricalcium Aluminate
C_3S	Tricalcium Silicate
C_4AF	Tetracalcium Aluminoferrite
$Ca(OH)_2$	Calcium Hydroxide
Ca^{2+}	Calcium Ion
$CaCl_2$	Calcium Chloride
$CaCO_3$	Calcite
$(CaMg)CO_3$	Dolomite
CANMET	Canada Center for Mineral and Energy Technology
CH	Calcium Hydroxide
Cl	Chlorine
Cl^-	Chloride Ion
CMA	Calcium Magnesium Acetate
C-N(K)-S-H	Calcium-Alkali-Silicate-Hydrate
CO_2	Carbon Dioxide
CSH	Calcium Silicate Hydrate
DOT	Department of Transportation
EDS	Energy Dispersive Spectrometry
EMPA	Electron Micro-Probe Analysis
ESEM	Environmental Scanning Electron Microscope
F-T	Freeze-Thaw
GGBFS	Ground Granulated Blast Furnace Slag
K	Potassium

Table of Acronyms

Acronym	Definition
MBAP	Magnesium Chloride Based Agricultural Product
MDOT	Michigan Department of Transportation
Mg	Magnesium
$Mg(OH)_2$	Brucite
Mg^{2+}	Magnesium Ion
$MgCl_2$	Magnesium Chloride
MSH	Magnesium-Silicate-Hydrate
N(K)-S-H	Alkali-Silicate-Hydrate
NaCl	Sodium Chloride
OH^-	Hydroxide Ion
psi	Pounds per Square Inch
RCPT	Rapid Chloride Permeability Test
SCM	Supplementary Cementitious Materials
SDDOT	South Dakota Department of Transportation
SEM	Scanning Electron Microscopy
SHA	State Highway Agency
SHRP	Strategic Highway Research Program
vpm	Vibrations per Minute
w/c	Water-to-Cement Ratio
w/cm	Water-to-Cementitious Ratio
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

Problem Statement

Keeping roads safe and passable are key concerns for any State Highway Agency (SHA), especially during the winter season when ice and snow accumulation on roads and bridges can create hazardous driving conditions. To accomplish this, SHAs are constantly seeking out, evaluating, and adapting new winter maintenance strategies that are cost effective and environmentally friendly. One such area where new strategies are being employed is the broad area of deicing and anti-icing. Deicing is defined as any effort to remove ice from road and bridge surfaces after ice deposition has occurred. This is in contrast to anti-icing, which is defined as a surface treatment applied prior to ice formation that eliminates ice accumulation or facilitates ice removal by lessening the bond between the ice and the riding surface. In general, deicing and anti-icing are accomplished through the use of various chemicals including aqueous solutions of chlorides (e.g. magnesium chloride, sodium chloride, and calcium chloride) or other chemicals such as calcium magnesium acetate and urea. Although the efficacy of these chemicals for deicing and anti-icing has been clearly demonstrated, possible detrimental effects to concrete in transportation structures have not been fully examined and documented. In this sense, the true cost effectiveness has not been determined as chemical attack on concrete is a possibility and in turn, the resulting deterioration of the structures from chemical attack may lead to costly rehabilitation or replacement. Based upon published research, the most problematic chemicals appear to be the chlorides of magnesium, calcium, and sodium and other chemicals containing calcium and magnesium (e.g. calcium magnesium acetate). Use of these chemicals has increased given their relatively low cost, ease of use, and effectiveness for deicing and anti-icing, in certain applications. Use of alternative chemicals such as propylene glycol and ethylene glycol have seen limited use given concerns about their environmental impact, whereas potassium acetate, sodium acetate, potassium formate, and sodium formate are used almost exclusively on airports (with some use in automated bridge deicing systems) due to high cost. In the end, chloride-based deicers appear to be the best choice for highway applications if they can be used in such a way as to minimize possible chemical attack to concrete.

The degradation of concrete used in pavements and bridges that may occur as a result of attack by chemical deicers/anti-icers is the result of an increased concentration of dissociated calcium and magnesium ions in the concrete pore water. In theory, these free ions are available to combine with materials in the concrete to form expansive or weak reaction products such as brucite or magnesium silicate hydrates, respectively. Of course, the dissociation of chlorides into ionic species also increases the concentration of chloride in the pore water solution, which has been well documented as a primary cause of scaling and corrosion of reinforcing steel. These possible and known effects must be fully understood if these chemicals are to be used as a mainstay of any deicing or anti-icing strategy. The goal of this proposed research is to examine the effects of deicing and anti-icing chemicals on portland cement concrete and to recommend changes to concrete mixture designs, construction practices, and winter maintenance procedures that will make these solutions non-detrimental to concrete durability.

Summary of Project Tasks

Task 1: Literature Review
Task 2: Conduct Survey
Task 3: Site Selection
Task 4: Meeting with Technical Panel
Task 5: Characterization of Field Specimens
Task 6: Laboratory Experiment
Task 7: Assessing and Minimizing the Impact of Deicing/Anti-Icing Chemicals
Task 8: Effects of Various Deicing/Anti-Icing Chemicals
Task 9: Life Cycle Cost Analyses
Task 10: Development of Guidelines
Task 11: Submit Interim Report
Task 12: Meeting With Technical Panel at Michigan Tech
Task 13: Prepare and Submit Final Report
Task 14: Executive Presentation to Research Panel
Task 15: Executive Presentation to SDDOT Executive Review Board

Report Organization and Distribution

The final report for this project is extensive. To facilitate distribution, the report has been broken down into a number of separate volumes and these are listed below.

- **Executive Summary** – Provides a concise overview of the entire project.
- **Final Report** – The final technical report organized into nine sections.

  Section 1 - A brief introduction
  Section 2 - An abridged background for the project based on the Task 1 literature review
  Section 3 - Presents the experimental approach for the entire project
  Section 4 An abridged summary of the Task 5 results
  Section 5 - An abridged summary of Task 6 laboratory results for Phase I and Phase II
  Section 6 - Presents a discussion of the results of Tasks 5, 6, 7, 8 and 9
  Section 7 - Presents suggested mitigation strategies based upon the results of this study
  Section 8 - Conclusions based upon the results of this study
  Section 9 - Recommendations based upon the results of this study
  Section 10 - Bibliography used as the basis for Section 2

- **Appendix to Final Report** – The appendix contains details on specific analytical methods used in the study. Also, the appendix contains an unabridged summary of results for the characterization of field specimens and for all laboratory experiments.
- **Full Literature Review** – Provides the unabridged version of the literature review.
- **Guidelines** – A practical guideline document to assist DOT personnel in implementing this research.

1.0 Overview

The purpose of this literature review is to summarize past research efforts regarding damage resulting from the use of various deicing agents on concrete transportation structures. In order to understand the potential damage that deicers may cause, this literature review discusses the following topics:

- Concrete properties (i.e. permeability, aggregates, and air content) and their impact on concrete resistance to freeze-thaw and deicer attack.
- Physical interactions that occur in the concrete as a result of freeze-thaw cycling in the presence of deicing chemicals.
- Chemical interactions between deicing chemicals and concrete and how they complicate the physical interactions.
- Deleterious effects that deicing chemicals have on both the hydrated cement paste and the aggregate.

1.1. Concrete Properties that Affect Freeze-Thaw and Chemical Resistance

To better understand the effects that freeze-thaw cycles and deicing chemicals have on concrete, it is important to have a working knowledge of the basic properties of concrete. The most prominent characteristics to control are: permeability; air content; cement chemistry; aggregate properties; and cracking. In addition, it is necessary to understand the physical and chemical interactions that take place on the surface and within the hardened cement paste.

1.1.1 Cement Chemistry

The major constituents present in cement are impure phases of the four compounds: tricalcium silicate (C_3S)[1], dicalcium silicate (C_2S)[1], tricalcium aluminate (C_3A)[1], and tetracalcium aluminoferrite (C_4AF)[1]. These chemical compounds form at high temperatures within the kiln just before and during the clinkering process. The calcium silicates make up approximately "three-fourths of the cement and are responsible for the cementing qualities" (Mindess et al. 2003). When mixed with water, the cement undergoes a series of chemical reactions that ultimately hardens the cement into hydrated cement paste. These reactions are commonly referred to as hydration and the hardened cement paste as hydration products (Mindess et al. 2003).

In portland cement, the compounds "contain small impurities of the oxides present in the clinker" (Neville 1997). Impure C_3S and C_2S are referred to as alite and belite, respectively. It is known that alite reacts more rapidly than belite, contributing to high early strength, whereas belite is responsible for the ultimate strength. The two major hydration products are calcium silicate hydrate (CSH)[1] and calcium hydroxide ($Ca(OH)_2$). Potential problems that can arise with these hydration products due to the application of deicing chemical are discussed later.

One way to mitigate problems with deicing chemicals is to partially replace portland cement with supplementary cementitious materials (SCMs) such as fly ash, silica fume or ground granulated blast furnace slag (GGBFS). The use of SCMs has many benefits, including their

[1] For phases in cement clinker and hydration products in hardened cement paste, ceramic notation is used to identify chemical components in these phases. In this notation: C = CaO, S = SiO_2, A = Al_2O_3, H = H_2O, and F = Fe_2O_3.

influence on lowering the heat of hydration and improved strength gain over time. More importantly, they aid in the resistance of concrete to chemical attack by improving the chemical nature and microstructure of the hydrated cement paste by decreasing the amount of calcium hydroxide through the pozzolanic reaction and decreasing permeability (Neville 1997).

1.1.2 Permeability

It is widely understood that the water-to-cement ratio (*w/c*) has the largest influence on the durability of concrete. When SCMs are used this is referred to as the water-to-cementitious (*w/cm*) ratio (*note*: unless otherwise specified, the terms *w/c* and *w/cm* can be used interchangeably in this discussion). By having a relatively low *w/c*, the porosity of the hardened concrete will decrease and in turn, be stronger and have lower permeability. Porosity is a "measure of the proportion of the total volume of concrete occupied by pores" (Neville 1997). Concrete having lower permeability is the more durable because permeability of concrete "controls the rate of entry of moisture that may contain aggressive chemicals (i.e. chlorides) and the movement of water during heating or freezing" (Mindess et.al. 2003). Therefore, a lower *w/c* ratio increases strength and improves resistance to cracking from the internal stresses generated by adverse reactions.

In addition, the *w/c* ratio affects the volume of capillary pores that form as the cement paste hydrates (i.e. volume increases significantly for *w/c* ratio > 0.42). Permeability is therefore controlled by an interconnecting network of capillary pores. During hydration, the capillary network becomes increasingly tortuous as interconnected pores are blocked by the formation of hydration products, most notably calcium silicate hydrate. Calcium hydroxide also continues to grow within the residual pores, forming impermeable regions. At a given degree of hydration, "the time at which complete discontinuity of the capillary pores occurs is a function of the *w/c* ratio," (Mindess et al. 2003). Furthermore, permeability decreases as the cement continues to hydrate over time. Some authors have classified the pore size into classes according to the pore hydraulic radius. Thus, the pore size is classified as micro gel pores (1 nm), meso gel pores (30 nm), micro capillarities (1 μm), meso capillarities (20 μm) and macro capillarities (1 mm) (Setzer 1997).

Although the bulk hardened cement paste has the largest influence on permeability, it is also significantly influenced by the paste-aggregate interface (Neville 1997 and Mindess et. al. 2003). Cracking at the paste-aggregate interface increases permeability, creating pathways for the flow of water. In addition, substantial hydration and a low *w/c* ratio, all contribute to a more impermeable concrete and enhance resistance to freeze-thaw damage (Neville 1997). In order to ensure the resistance of newly placed concrete to alternating freezing and thawing cycles, it is desirable to allow the concrete to cure completely before exposing it to harsh winter conditions. In certain cases even after complying with all these requirements, the leaching of calcium hydroxide (which constitutes up to 20% of the concrete matrix) due to concrete exposure to acidic or highly concentrated salt solutions will decrease the strength and increase the porosity of the concrete, affecting the long term durability (Carde and Francois 1997). Also, continuous exposure to water, especially that containing dissolved carbon dioxide (CO_2), will cause dissolution of calcium hydroxide, but it is a much slower process where precipitation and dissolution of ettringite and calcium silicate hydrate dissolve over time (Haga et al. 2005). The beneficial effect of a low *w/c* ratio is also reflected in the speed of dissolution of calcium hydroxide as specimens with a high *w/c* ratio have larger

pore volume, thus leach calcium hydroxide faster (Haga et al. 2005). In addition, after extensive dissolution of calcium hydroxide, decalcification of calcium silicate hydrate due to removal of interlayer calcium ions can induce shrinkage of the paste causing cracks and affecting the connectivity of pore structure (Chen et al. 2006). The importance of calcium silicate hydrate decalcification on the increase in porosity and loss of strength has been considered negligible if compared with the contribution made by the dissolution of calcium hydroxide; that is, leaching of calcium hydroxide produces macroporosity that accounts for up to 70% of strength loss while decalcification of calcium silicate hydrate produces microporosity that accounts for only 6% of strength loss in portland cement paste (Carde and Francois 1999).

1.1.2.1 Chloride Diffusion

One important aspect of concrete permeability regarding the application of deicing chemicals is chloride diffusion. Diffusion is a process by which a fluid permeates a porous material such as soil or concrete. The surface concentration is the principal factor for chloride diffusion in near-saturated concrete (Mindess 2003). However, the movement of chloride in concrete is also a function of several variables. These include pore size and spacing, pore volume fraction, changes in pore size with respect to location within the cement paste, and structure of phases present in the pore system.

To mathematically describe the process of one-dimensional chloride migration, Fick's Second Law of Diffusion is often used for most concrete applications.

$$C_{d,t} = C_0\left[\left(1 - erf\,\frac{d}{2\sqrt{D_c \times t}}\right)\right] \tag{1.1}$$

The variables described in the equation are defined as the following:

- C is the chloride concentration at a depth, d, and a time, t.
- C_o is the chloride concentration at the surface of the concrete, where the chlorides are being applied, usually as deicers.
- *erf* is the abbreviation for the error function
- D_c is the diffusion coefficient, which expresses concrete resistance to chloride diffusion, also related to concrete permeability and the moisture content (Mindess 2003).

Equation 1.1 can be used to calculate the diffusion parameters C_0 and D_c and to estimate chloride ingress in concrete, thus future changes in chloride concentration can be predicted at any depth from the concrete surface over any period of time. With such predictions, effective strategies to mitigate damage from chloride ingress can be implemented.

Previous research has described the physics of chloride diffusion through saturated cement paste as a Fickian diffusion mechanism combined with a Langmurian adsorption equilibrium process (Pereira 1984). This closely illustrates the action of ionic species penetrating the surface of concrete and migrating into the material's pore structure (Papadakis 1996). The rate of chloride diffusion is usually altered by the reversible process of adsorption and de-sorption of the ions to the hydration products of the matrix and by the binding of chlorides to

the hydration products, particularly calcium silicate hydrate. Further, a considerable amount of the damage in cement paste exposed to a brine results from the interaction of ions with calcium silicate hydrate since it is the dominant phase in most hydrated cements (Kurdowski 1995). Other evidence of chloride binding is the fact that chlorides may be removed from the mix water via binding to the primary phases, present in the cement paste (Mondal 1975, Jeffery 1952, Barnes 1980, Colville 1971, 1972), and this occurs during the initial set (Lambert 1985).

Additionally, certain ionic species may also get "trapped" (*i.e.* chemically and physically bound) in the structure of the hydration products, reacting to form new phases that may be non-cementitious in nature. The total amount of bound chlorides will depend on the accompanying cation. For instance, the amount of bound chlorides has been found to be higher for calcium chloride and magnesium chloride than for sodium chloride (Pavlik 2000, Arya et al. 1990). An increase in chloroaluminate formation in samples exposed to $CaCl_2$ has been considered the reason for this behavior (Arya et al 1990) as calcium chloroaluminate will bind considerable amounts of free chloride diffusing through the pore fluid (Lambert et al. 1984). calcium silicate hydrate may also bind some chloride in the interlayer sheets and at the surface, referred to as chemisorbed chloride (Beaudoin 1990). Different methods are used to determine the bound chloride in cement paste. In one method, the pore solution is expressed, or squeezed out of the concrete specimen for chemical testing (Tritthard 1989).

In some cases, phase formation is expansive and can induce severe stress concentrations and failure as a result. Unfortunately, stress-expansion models that predict the effect of this induced stress for life prediction of structures are not available at this time (Piltner and Monteiro 2000). The most well known phase observed as a result of the dissolution-precipitation reaction with magnesium is magnesium hydroxide, also known as brucite ($Mg(OH)_2$) (Hofmeister 1992). Magnesium silicate hydrate (MSH), a non-cementitious by-product, is another common phase that has been observed to form and cause damage in concrete exposed to magnesium-based deicers (Lee 2000). (The formation of these by-products and other detrimental effects will be discussed further in section 1.2.2.2 Effects of Magnesium Chloride).

Fick's Second Law has served as the basis for assessing diffusion in concrete by various methods. The basic technique is to expose a sealed concrete sample (cubic, prismatic, or cylindrical in shape) to an aqueous solution at a fixed chloride concentration and then after some time *t*, measure the chloride concentration at various depths. The minimum duration of exposure is 35 days according to ASTM C1556, *"Test Method for Determining the Apparent Chloride Diffusion Coefficient of Cementitious Mixtures by Bulk Diffusion"*. In this test method, the sample is sectioned with a diamond blade or ground with an abrasive perpendicular to the direction of chloride ingress. The concentration of chlorides in each section (i.e. in the dust sample obtained at each depth) is measured, and the data is used to generate a concentration-depth profile for the flow of chlorides in one direction. Based on those measurements, equations derived from Fick's second law are applied to calculate the diffusion coefficient. The diffusion coefficient has been found to be correlated with the exposure temperature and *w/c* ratio; the effective diffusivity increases with *w/c* ratio and temperature (Page et al. 1981). Today, advanced technology has made it more practical to determine the concentration of chlorides with depth by using such equipment as X-ray fluorescence (XRF), scanning electron microscopy (SEM), wet chemistry, X-ray microscopy,

or electron probe micro-analysis (EPMA), as well as diffusion cells (Andrade 1992, Yu 1993, Sutter 2003).

All concrete regardless of age contains a small number of cracks that are present in the hydrated cement paste and in the interface between the hydrated cement paste and both fine and coarse aggregates (Mehta 1993). The void space in the local vicinity of these cracks provides easy pathways for the transport of water and aggressive chemicals, thereby impacting the rate of diffusion of each(Gerard 2000). The recent development of theoretical and mathematical models, taking the effects of cracking into consideration, can more accurately predict the rate of chloride ingress through cement paste (Boulfiza 2003). These, like most other mathematical models for diffusion in concrete, usually consider the physics of water transport as the basis for the calculation of the overall amount of chloride ingress over time (Yunping 1994). A working knowledge of the rate of ion ingress is extremely useful for determining the long-term durability of a structure (Costa 1999, Mangat 1994, QCL Group *Australia* 1999). Also, by determining the rate of ionic transport, the initial corrosion of reinforcing steel embedded in structural concrete can be predicted (Mangat 1987, Suryavanshi 1998).

In addition, other concrete-making materials may also affect the overall diffusivity of concrete. Most practical concrete is not made exclusively with portland cement, aggregate, water, and air-entrained admixture, but also contains SCMs and chemical admixtures (Rezansoff 1988, Rosskopf 1975). Most modern concretes contain SCMs such as fly ash, GGBFS, or silica fume, as well as others. The addition of SCMs is usually done to enhance performance in freeze-thaw environments, improving structural durability (Bleszynksi 2002). Regarding the diffusion of chlorides, nearly all SCMs used today including fly ash, GGBFS, and silica fume, have been shown to significantly reduce the rate of diffusion of chlorides in cement (Byfors 1987, Stark 1997, Thomas 1999, Bentz 2000, Bleszynski 2002). The use of pozzolanic cement (cement pre-blended with a pozzolanic SCM) has been found to decrease the penetration of chloride ions into cement paste and concrete even though no changes in total porosity were observed that could be correlated with this greater resistance (Collepardi et al. 1972). Other admixtures are applied as surface coatings, and some of them actually alter the physical properties of concrete, including its conductivity and capacity to transmit heat. With respect to deicing, this could potentially save money (Yehia 2003).

In summary, the diffusion of ionic species through the matrix of concrete is a very complicated problem that has many variables. Although diffusion in concrete has been studied extensively, methods to measure and apply finite and precise diffusion coefficients that could help predict the long-term durability of a given structure have not yet been developed (Yunping 1994, Truc 2000). The mathematics and physics of transport mechanisms in concrete essentially remain unsolved. Future research in this area would aid in the understanding of ionic diffusion into concrete due to the application of aggressive deicing chemicals as are commonly applied to roads and bridge decks in northern regions of the United States.

1.1.3 Air Content

Increasing the air content of concrete through air entrainment has been found to improve its frost resistance (to a point), but at the expense of lowering its strength (Figure 1.1). In fact, "a strength loss of 10-20% occurs in air entrained concretes" (Mindess et al. 2003). However, to have good frost protection, air entrainment is required.

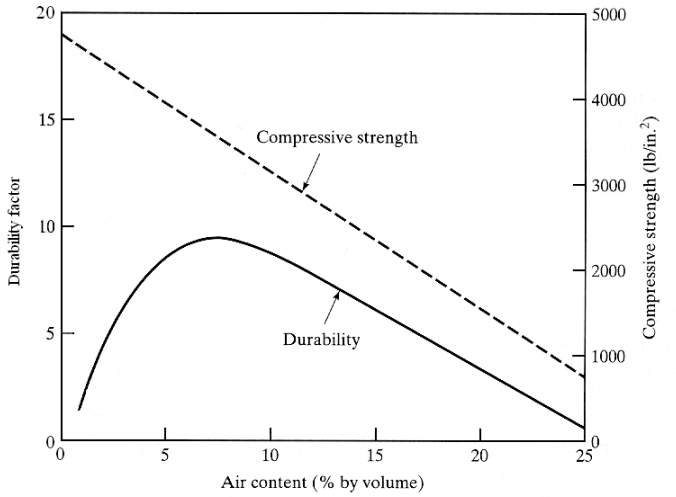

Figure 1.1. Effect of entrained air on durability and strength.

The required air content is based on the maximum aggregate size, with less air required when larger aggregates are used as shown in Table 1.1 (ACI 201.2R 1992). This reduction in required entrained air reflects that with all things held equal, there is less mortar present in concrete made with larger coarse aggregate and less total air is needed to protect it. The closely spaced entrained air voids "protect concrete during freezing by providing reservoirs for water that exits from the paste on freezing" (Mindess et al. 2003). However, the spacing of air voids depends on the *w/c* ratio (i.e. the higher the *w/c* ratio, the larger the air-void spacing and the lower the specific surface). It has been found that "a higher specific surface, which corresponds to smaller air voids, is desirable so as to minimize the adverse effect of air" on the strength of concrete (Neville 1997). In addition, research indicates a maximum value for air void spacing and the minimum value of the specific surface of the air in concrete in order to ensure the presence of an adequate air-void system. This provides adequate protection from freezing and thawing with the least amount of strength loss. Section 1.2.1 describes in detail the theories regarding the mechanism(s) by which entrained air voids protect concrete from physical damage due to freezing and thawing. Other advantages of increasing the air content in concrete include resistance to scaling caused by deicing salts.

Table 1.1. Effects of *w/c* ratio on the air void system in concrete (Mindess et al. 2003)

w/c ratio	Air Content (volume %)	Spacing Factor in [mm]	Linear Expansion per Freeze-Thaw Cycle (%)
0.35	4.8	0.0043 [0.11]	0.00004
0.45	4.7	0.0055 [0.14]	0.00014
0.55	5.2	0.0059 [0.15]	0.00021
0.65	4.9	0.0071 [0.18]	0.00026

1.1.4 Aggregate Properties

Aggregates that are susceptible to freeze-thaw damage can be reduced in size to improve resistance and durability. Susceptible aggregates cause widespread concrete deterioration in the form of "pop-outs" on the surface of pavements (Mindess et al. 2003). Aggregates that may suffer pop-outs generally are fine-grained, have high total porosity and are virtually impermeable. When these types of aggregates become "saturated, the critical size of the rocks can become less than the size present in the aggregate" (Mindess et al. 2003). Generally, fracture of the aggregate occurs, leading to pop-outs at the surface.

D-cracking aggregates share similar properties to those susceptible to pop-outs. Moisture accumulates at slab joints or cracks, seeping down into the concrete and saturating the susceptible aggregates. When this moisture freezes it expands, resulting in fracturing of the aggregate. Thus begins the deterioration process as the concrete is subjected to repeated freezing and thawing cycles (Mindess et al. 2003). This is discussed further in the next section.

While these problems are due to physical attack, other types of damage result from chemical interactions. For example, reactions between silica in aggregates and alkalis contained in the pore solution have deleterious effects referred to as alkali-silica reactivity (ASR). The overall reaction is a complex process. Fundamentally, the alkali-silica reaction will "result in the production of two-component gels – one component is a non-swelling calcium-alkali-silicate-hydrate [C-N(K)-S-H] and the other is a swelling alkali-silicate-hydrate [N(K)-S-H]. The alkali-silica reaction will be safe if only the non-swelling C-N(K)-S-H forms, but unsafe if both gels form" (Mindess et al. 2003).

1.1.4.1 Dedolomitization

Another type of deleterious chemical reaction was published by Cody and Spry (1994). In their study, they examined a particular type of aggregate and its susceptibility to chemical attack by magnesium based deicers. They presented the two ways in which magnesium is introduced into the cement paste. One way is through the application of magnesium-based deicers on pavement surfaces. The other way is dependant on the type of aggregate used in concrete. In their findings, Cody and Spry (1994) identified a dolomite coarse aggregate that undergoes dedolomitization would produce magnesium, which then migrates to the cement paste.

Using a petrographic microscope, scanning electron microscope, and electron microprobe to determine the differences, Cody and Spry investigated both durable and non-durable concrete containing dolomite rock. It was found that the aggregates in the non-durable or short-service life (less than 15 years) concrete had poor performance due to the fine-grained structure that contained "numerous euhedral and subhedral dolomite rhombohedra, and relatively high porosity" (Cody & Spry 1994). These aggregates were "found to have undergone pervasive chemical reactions with the cement which produced reaction rims on the boundaries of the coarse aggregate particles and in the cement region adjacent to aggregate boundaries" (Cody & Spry 1994).

In contrast, dolomite aggregate in the durable concrete was "coarse-grained, tightly interlocked crystal fabric, anhedral dolomite boundaries, and low porosity" (Cody & Spry 1994). The specimens of durable concrete were extracted from highways that have been in

service longer than 40 years. The durable concrete exhibited no remarkable deterioration. Therefore, "textural and porosity differences are believed to be chiefly responsible for different service lives of the two groups of concrete" (Cody & Spry 1994).

The reaction identified within the non-durable concrete was generally referred to as alkali-carbonate reactivity (ACR) that occurs between the dolomite coarse aggregate and cement pore solution. This reaction occurs when dolomite from the aggregate is attacked by alkali from the high pH pore solution (see Equation 1.2 below). Consequently, magnesium and carbonate ions are released into the pore solution. The magnesium ions precipitate as brucite, (see Equation 1.2 below) as the carbonate ions react with calcium hydroxide from the cement to form calcite, $CaCO_3$ and hydroxide ions (see Equation 1.3 below). The formation of brucite and calcite cause crystal growth pressures among other processes (e.g. hydration state changes of magnesium chloride hydrates) that lead to expansion of the concrete causing premature failure (Cody & Spry 1994).

$$CaMg(CO_3) + 2OH^- \rightarrow CaCO_3 + Mg(OH)_2 + CO_3^{2-} \quad (1.2)$$

$$CO_3^{2-} + Ca(OH)_2 \rightarrow CaCO_3 + 2OH^- \quad (1.3)$$

Cody and Spry identified the ultimate cause of concrete deterioration as the alkali-dolomite reaction. However, they also concluded "the reaction itself does not produce deterioration". It is actually environmental changes, such as slight volume expansions that cause weakening of the aggregate-paste bonding and micro-cracking. In addition to these findings, "there was no evidence of complete dedolomitization" (Cody & Spry 1994) on any of the reaction rims of test specimens. Therefore, even partial dedolomitization may potentially lead to deterioration.

Furthermore, concrete containing such reactive dolomite aggregate may be more susceptible to deicer (i.e. $MgCl_2$, $CaCl_2$, NaCl) deterioration under actual winter highway conditions. The presence of chloride brines at aggregate-paste boundaries may be especially damaging if bonding at the boundary has already been weakened by dedolomitization and microcracking. Repeated freezing and thawing conditions will enhance deterioration on roads where deicers are used abundantly. Other studies indicate that concrete, containing aggregate that reacts adversely with the concrete pore solution may be susceptible to enhanced deterioration when exposed to deicing chemicals (Dubberke & Marks 1985).

1.1.5 Cracking

Although cracking may not cause immediate structural failure, it may provide the onset for deterioration that ultimately leads to failure. As cracking spreads, it increases the permeability of concrete, leading to surface scaling and further internal stress-related cracking. Table 1.2 lists the leading causes of cracking in concrete due to interactions with its surroundings (Mindess et al. 2003).

Cracking results from various contributing factors. One factor is the loss of water in fresh concrete, which leads to surface cracking. This is due to evaporation at the concrete surface, or suction of water by the subbase or formwork materials, or both. The removal of water from the paste will "generate negative capillary pressures, which will cause the volume of the paste to contract" (Mindess et al. 2003). As the pressures continue to rise within the paste, plastic shrinkage results, leading to differential volume changes, which in turn, "cause cracking under induced tensile stresses" (Mindess et al. 2003). Other types of shrinkage

include drying shrinkage, autogeneous shrinkage, and carbonation shrinkage. Drying shrinkage is controlled by creating contraction joints in pavements and slabs. These joints prevent uncontrolled shrinkage cracking from occurring across the surface of the concrete by confining it to the area where the joints are located. An autogenous shrinkage result, due to water loss associated with the formation of hydration products themselves, and is generally thought to be of consequence only when the *w/c* ratio drops below 0.40. It is worth noting that shrinkage is a paste property; the aggregates present within the concrete restrain volume changes that are occurring within the paste.

Table 1.2. Causes of cracking in individual components of concrete due to interactions with surroundings (Mindess et al. 2003)

Component	Type	Cause of Distress	Environmental Factor(s)
Cement	Unsoundness	Volume expansion	Moisture
Aggregate	Temperature cracking Alkali-silica reaction D-cracking	Thermal stress Volume expansion Hydraulic pressure	Temperature Supply of moisture Freezing and thawing
Cement paste	Plastic shrinkage Drying shrinkage Sulfate attack	Moisture loss Volume expansion	Wind and temperature Relative humidity Sulfate ions

The cracking discussed thus far is visible with the naked eye, and is therefore referred to as macrocracking. But all cracking initiates at a micro-level with microcracks, which can only be seen with the aid of a microscope, coalescing into macrocracks as failure occurs. Microcracks are very fine cracks that can occur at the interface of the aggregate and cement paste or in the paste itself. This type of cracking may result from "differences in the mechanical properties between coarse aggregates and the hydrated cement paste" (Neville 1997). Microcracking has been known to result from freeze-thaw cycling, as hydraulic and osmotic pressures build up within the hydrated cement paste. This is discussed further in the next section.

As previously mentioned, D-cracking is a type of cracking that initiates in coarse aggregates susceptible to freeze-thaw damage, and is most often associated with concrete highways and other pavements. It has been defined as "cracking in a slab surface in a pattern that appears first in an orientation parallel to transverse and longitudinal joints and cracks, continues around corners, and may progress into the central area of the slab" (Girard et al. 1982).

1.2. Types of Interactions

Both physical and chemical interactions occur within concrete when it is exposed to freeze-thaw conditions and deicing chemicals. Physical interaction is initiated when the saturated concrete freezes, subjecting the concrete to volume change and the development of internal stresses that are amplified by the presence of deicer ions in the pore solution and the thermal shock that occurs as ice is melted. Chemical interaction results from the application of deicing chemicals, leading to possible degradation of the concrete structure. Combined, physical and chemical interactions disrupt the concrete properties previously discussed.

1.2.1. Physical Mechanisms of Paste Freeze-Thaw Attack

Saturated concrete subjected to freeze-thaw conditions can undergo damaging internal physical alterations as pressure develops from ice formation within the pore system. Both the hydrated cement products and aggregates can be vulnerable to freeze-thaw damage, which will produce microcracking and ultimately surface scaling and deterioration. The application of deicing chemicals tends to increase the magnitude of physical deterioration by increasing the development of internal pressures.

At least three separate theories have been forwarded to describe the actions taking place inside the hydrated cement paste during freezing. The most well known theory, the hydraulic pressure theory, was proposed by T.C. Powers in 1949. The process of the hydraulic pressure theory is illustrated below in Figure 1.2.

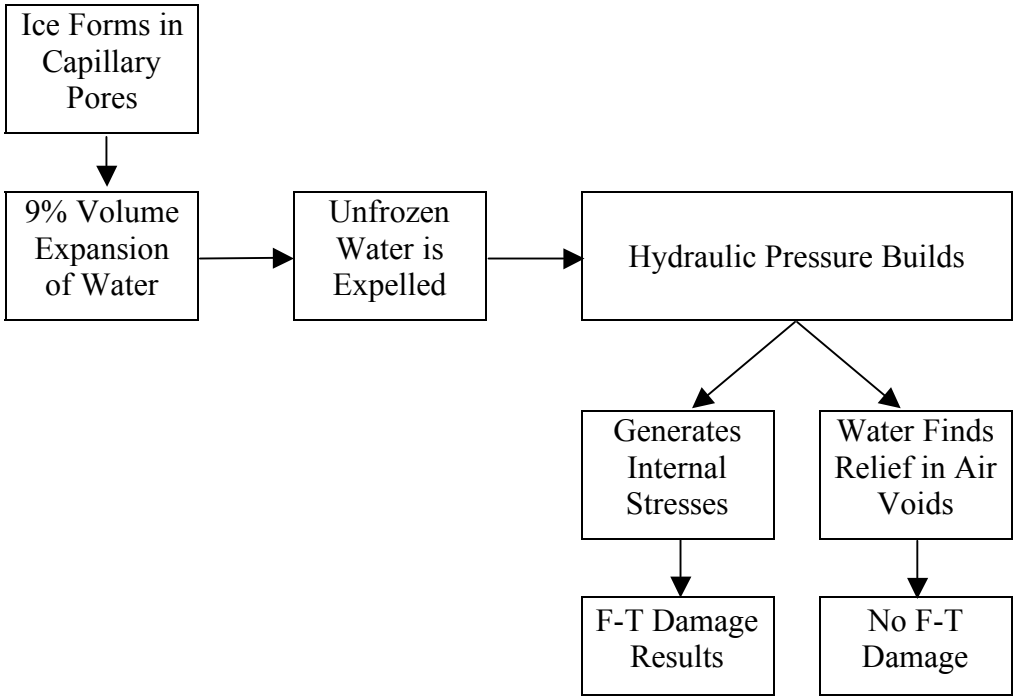

Figure 1.2. Schematic representation of the hydraulic pressure theory.

The phenomenon described by the hydraulic pressure theory begins as the temperature decreases below 32 ºF [0 ºC], gradually freezing water in the largest capillary pores first. The 9 percent volume expansion that results as ice forms forces the unfrozen water out of the pores. Hydraulic pressures build in resistance to the outward flow of water, generating excessive internal stresses that will fracture the hydrated cement paste if its strength is exceeded. However, when expelled water is able to find relief at entrained air voids within the cement matrix, it freezes there and damage is avoided.

Powers (1975) forwarded the osmotic pressure theory to address some limitations observed in the hydraulic pressure theory. This theory considers osmotic potential to be the primary cause of paste freeze-thaw damage and partially explains the amplifying deleterious effects of deicing chemicals. The combined affects of surface forces and the alkalinity of deicing salts lower the freezing point of the pore solution. Then only pure water forms ice and that is only in the larger pores, raising the alkaline concentration in the remaining pore solution and

thus lowering the freezing point. The difference in ionic concentration, or chemical potential, between the more highly concentrated solution remaining in the larger pores and the solution in the smaller pores causes solution migration to larger pores where the ionic concentration is higher. This migration generates osmotic pressure. This theory also explains why air-entrained paste contracts as it freezes, rather than expanding, even as ice continues to develop in the capillary pores as the temperature decreases below 32 ºF [0 ºC] (Marchand et al. 1994).

Hydraulic pressure and osmotic pressure are not the only causes of damage to hydrated cement paste exposed to frost action. According to a recent theory, analogous to the formation of ice lenses in soil, the capillary effect involving large-scale migration of water from small pores to large cavities is believed to be the primary cause of expansion in porous bodies (Mehta and Montiero 2006). In another theory advanced by Litvan (1975), the water held rigidly by the calcium silicate hydrate in cement paste cannot rearrange itself to form ice at the normal freezing point of water because the mobility of water existing in an ordered state is rather limited. Generally, the more rigidly water is held, the lower the freezing point. A relationship between pore size and freezing/melting temperature has been formulated based on thermodynamics (Kaufmann 2000).

As discussed, limiting the average entrained air void spacing to 250-300 μm can prevent the deleterious expansion of cement paste upon internal ice crystallization (Powers and Helmuth 1953). In fact, experimental results show that non-air entrained concrete expands upon freezing whereas adequately air-entrained paste contracts upon freezing, because ice crystals on the surface of the air voids draw water from the surrounding porous matrix.

The transformation of ice from liquid water generates a volumetric dilatation of 9 percent, a fact that has been central to all previous theories. However, more recent theories attribute the damage from freezing of concrete to be the result of crystallization pressure (Valenza and Scherer 2005; 2006; 2007). The stress exerted on porous bodies by crystals of salt or ice follows from the fact that the solids repel one another. There is a film of liquid (thickness δ) separating the surfaces of the growing crystal and the pore wall, reducing the interfacial energy. The Van der Waals forces of ice alone provide a large enough repulsive force to exceed the tensile strength of concrete and push ice into contact with mineral surfaces. To avoid destructive pressure from the growth of ice in the pores, entrained air voids are provided as nucleation sites for ice. This occurs as crystals in the voids draw liquid from the small pores of paste (pore radius r_P<50 nm), and thereby impose compressive stresses on the concrete. The melting point (T_m) of a crystal with a radius of curvature, *r*, is given by the Gibbs-Thomson equation:

$$T_m(\kappa_{CL}) = T_m(0) - \frac{\gamma_{CL}\kappa_{CL}}{\Delta S_{FV}} \tag{1.4}$$

where γ_{CL} is the crystal/liquid interfacial energy, $\kappa_{CL} = 2/r$ is the curvature of the crystal/liquid interface, and ΔS_{FV} is the entropy of fusion per unit volume of crystal. $T_m(\kappa_{CL})$ is the threshold for forming crystals in capillary pores, where $\kappa_{CL} = 2/(r_P - \delta)$.

When the temperature T $< T_m(2/(r_p - \delta)$, the crystal will bulge into the mouths of intersecting pores (radius $r_E < r_P$) until the curvature satisfies Equation 1.4. To be in equilibrium, the pore wall imposes a confining pressure on the crystal's surface, which results in tensile stress along the pore wall. The confining pressure and tensile stress is proportional to the difference of the curvature of the confining pore and crystal surface. If excessive, this tensile stress will initiate microcracking and weaken the concrete during internal freezing (Valenza and Scherer, 2006).

The ice can exist in the capillaries and in the air voids simultaneously under a subcooling condition because of the suction in the pore fluid. The ice penetrates the pores until the curvature of the pore reaches $2/(r_p-\delta)$ at equilibrium. The penetration will draw the pore solution surrounding the void, compressing the porous concrete. This also explains why the volume of saturated concrete with air entrainment shrinks. As the temperature is further reduced, ice is able to access more of the pore space. Damaging stresses are produced under two possible situations: 1) ice escapes from a large void by passing a constriction; 2) ice grows into a zone of saturated microstructure encapsulated by the invading ice (Valenza and Scherer 2007).

Rösli and Harnik (1980) suggest that thermal shock occurs when frozen concrete surfaces are thawed by means of deicing salts. A large amount of heat is required to melt the ice cover and the concrete itself contributes much of this heat possibly resulting in the creation of a significant temperature gradient at the surface. It is also widely regarded that "stress induced in the surface layers by the thermal gradient can surpass the tensile strength of concrete and lead to microcracking" (Rösli and Harnik 1980). They also suggest that a "layer-by-layer freezing could lead to surface scaling. The outer layer of the concrete contains relatively little deicing salt as it is washed out by the liquid water at the surface. In that layer, ice can thus form at temperatures slightly below 32 ºF [0 ºC]. However, in the layer just beneath it, the salt concentration is high and freezing generally does not occur" (Rösli and Harnik 1980). The difference in salt concentration will create stresses due to different expansion of the two layers, leading to scaling (Rösli 1980, Marchand 1994, Pigeon 1995).

Resulting visual damage from these physical mechanisms of attack are most commonly scaling, map cracking, or paste disintegration. Internal microcracking caused by freeze-thaw damage will eventually progress to scaling on the surface of the pavement. Microcracking is usually first seen around joints, pavement edges, and cracks, since more moisture accumulates in these places. Once cracking begins, the damage gradually worsens, increasing the permeability of the concrete and thus its susceptibility to the further moisture ingress.

A factor that contributes to the amplifying effect deicers have on physical freeze-thaw damage is that deicers increase the saturation level of concrete, increasing hydraulic pressures. This behavior causes concrete subjected to deicer salt application to remain in a critically saturated state for longer periods of time, increasing the likelihood of damage. Because deicers do not penetrate concrete in a pure state, but are instead in an aqueous solution, the diffusion of the deicer solutions is said to be more efficient than the penetration of pure deicer (i.e. solid deicers) into water saturated concrete (Setzer 1997).

Physical degradation caused by NaCl is usually in the form of severe scaling when concrete is subjected to freeze-thaw cycling (Mu et. al. 2002). This type of degradation is primarily a result of the supercooling effect that occurs when NaCl reduces the freezing point of water in the concrete pores (Ghafoori and Mathis 1997). This reduces the immediate development of hydraulic pressures in the concrete as the water remains liquid as the temperature drops below 32 ºF [0 ºC]. However, when the supercooled pore water finally begins to freeze, it does so at a much faster rate, generating a "greater magnitude of hydraulic pressure" (Marchand et al. 1994). Another physical effect of NaCl in the pore solution near the concrete's surface is the development of increased osmotic pressure that occurs after or during freezing (Marchand et al. 1994).

In addition to the theories already discussed another physical mechanism that can help explain the cause of concrete scaling from the application of deicing salts is that of salt crystallization within the pores (Hansen 1963). It is hypothesized that the pore solution can become supersaturated as wetting and drying cycles concentrate salts in the pores (Harnik 1980, Mindess et al. 2003). Once crystallization begins, salt molecules are drawn out of smaller pores into the larger pores, inducing potentially harmful crystallization pressures (Ghafoori 1997). An estimation of the magnitude of the crystallization pressure resulting from salt crystal formation has been provided by Winkler and Singer (1972). In their research, they indicated that gypsum and halite crystal growth may exert pressures exceeding 29,000 psi [200 MPa].

In reality, it is likely that the combined increases in osmotic pressures, thermal stress, level of saturation, and salt crystallization, all contribute to scaling of concrete in the presence of deicer chemicals. As salt concentration increases, the osmotic pressures will also increase because of the higher chemical concentration in the pore solution. Further, thermal stresses will be produced due to the melting of the ice cover and salt crystallization may occur in the pores due to the wetting and drying cycles. Also, the increased level of saturation will provide more water for the generation of pressures. In combination, these mechanisms are far more physically damaging for concrete exposed to deicers when subjected to cyclic freezing and thawing than for concrete that was not exposed to deicers. From this physical attack point of view, studies have demonstrated that lower concentrations of deicers (between 2 to 4% by mass) are more damaging than concentrations outside this range (Harnik et al. 1980).

1.2.2 Chemical Mechanisms of Paste Freeze-Thaw Attack

As discussed, deicer scaling/deterioration is commonly thought to be primarily a form of physical attack, possibly resulting from a combination of factors (Mindess and Young 1981, ACI 1992b, Marchand 1994, Pigeon 1994, Pigeon 1995). Some researchers have stated that the presence of deicing chemicals, particularly salts, can magnify or amplify the same mechanisms that lead to freeze-thaw deterioration of the paste (e.g. hydraulic and osmotic pressures) (Ghafoori 1997). Contributing to this effect is the fact that pore water containing a relatively small amount of dissolved salts is more easily absorbed into capillary pores, resulting in increased saturation of the concrete (Pigeon 1995, Ghafoori 1997).

Although most research suggests that salt scaling is primarily a physical deterioration mechanism, some researchers feel strongly that chemical interactions may also be occurring. Marchand (1994) summarized this view stating that more attention should be paid to the chemical interaction between the deicing salts and cement paste hydration products. Recent research indicates that the chemical interaction between deicers and concrete may not be as benign as previously thought.

It is suggested that the calcium hydroxide dissolution process results in increased porosity at exposed surfaces, increasing the permeability of the concrete. This in turn increases the amount of water available to freeze at 32 ºF [0 ºC] due to increased pore size (Marchand, 1994). One study conducted by the Michigan Department of Transportation (MDOT) adds credence to this theory. Muethel (1997) confirmed through laboratory analysis that depletion of calcium hydroxide led to an increase in permeability and reduced alkalinity of the concrete in the vicinity of cracks and joints. The reduction in the concrete pH contributed to corrosion of reinforcing mesh in the jointed reinforced pavements.

It would be expected that factors leading to an increased permeability would be more prevalent at exposed concrete surfaces. In addition to contributing to surface scaling, concrete faces along joint or crack walls would also be adversely affected. A number of studies appear to support this hypothesis. The previously cited study conducted by the Michigan Department of Transportation (MDOT) observed that calcium hydroxide leaching was pronounced in concrete cores obtained at transverse crack locations in jointed reinforced concrete pavements from three different State routes (Muethel 1997). Visual surveys of the concrete pavement surface revealed localized deterioration and staining, while laboratory analysis confirmed that depletion of calcium hydroxide, increased permeability, and reduced alkalinity of the concrete, had occurred.

A study conducted for the Ohio Department of Transportation (ODOT) investigated the joint deterioration observed in many northern tier States (Munoz 1994, Munoz 1995). Termed "coning," this deterioration is characterized by concrete degradation at joints that progresses from the bottom of the slab upward. The exact cause of this deterioration is unknown, but it is speculated that more than one distress mechanism might be at work. Munoz states that dowel baskets may interfere with proper concrete consolidation, resulting in weaker concrete and increased porosity and permeability. This contributes to a chemical attack mechanism, with dissolution of the concrete paste considered the primary cause. Munoz explored the dissolution mechanism, stating that both the presence of dissolved salts and the velocity of solvent flow through the concrete are important factors. It is speculated that concrete at the joints has increased permeability, with accompanying relatively high solvent velocity. Additionally, potentially high carbon dioxide content in the solution from melted snow and other factors may lead to an increased solubility of the concrete.

A study by Jang (1993) found that the use of chemical deicers led to concrete degradation through both their anionic and cationic constituents. In addition to causing dramatic pH shifts, evidence also exists that deicers exacerbate the alkali-silica reaction, aggregate freeze-thaw deterioration (D-cracking), and deicer scaling of concrete.

The use of deicing chemicals has also been implicated in both alkali-silica reactivity (ASR), and alkali-carbonate reactivity (ACR). It is suggested that deicer use contributes to these deleterious reactions due to the increased alkalinity of the pore solution and concrete saturation mainly linked with the use of NaCl (Nixon 1987, Muethel 1997, Crumpton 1989, Gillott 1994). In addition, it has been suggested that the pH of the exposure solution is the main factor during chemical attack, as the lower the pH, the higher the increase in total porosity and the leaching front penetration (Delagrave et al. 1994). As pH drops below 10.7, not only will the calcium hydroxide dissolve but also the solubility of ettringite increases. The presence of chloride in solutions with low pH increases the leaching of calcium and in turn the total porosity of the paste (Delagrave et al. 1996). However, other authors suggested that it is not only the change in solubility of calcium hydroxide that is problematic, but also the precipitation of compounds that may increase or reduce the expansion of specimens (Beaudoin et al. 2001).

The following sections describe potential deleterious effects of NaCl, $MgCl_2$, $CaCl_2$, CMA and the more recently formulated $MgCl_2$ based agricultural products (MBAP).

1.2.2.1 Effects of Sodium Chloride

At one time, sodium chloride (NaCl), also called rock salt, was thought to be an environmentally friendly, non-corrosive deicer, and became the most commonly used deicer on the market (Ghafoori and Mathis 1997; McDonald and Perenchio 1997). Today, some of the detrimental chemical effects of NaCl deicer are better understood.

One interaction resulting from the long-term application of the popular chemical deicer sodium chloride is the dissolution of calcium hydroxide (Hoffman 1984, Ge'gout 1992, Gagne' 1992) as the solubility of calcium hydroxide increases in the presence of NaCl when compared with pure water and this effect increases the lower the exposure temperature (Glasser et al. 2005). Thus, the solubility of calcium hydroxide has been found to increase to 2.97 mmol/kg for a solution of 4.3% chloride concentration of NaCl (Theissing et al. 1978). The dissolution equation is stated as follows (Marchand 1994):

$$2NaCl + Ca(OH)_2 \rightarrow CaCl_2 + 2NaOH \quad (1.5)$$

When this occurs, increased porosity near the exposed concrete surface results, increasing the permeability of the concrete and enhancing the amount of ice formed near 32 ºF [0 ºC]. Other authors support the view as that calcium hydroxide dissolution is not the main problem per se as compared to the exacerbation of other attacks such as chloride penetration, freeze-thaw and carbonation (Brown and Clifton 1988). In addition, soluble calcium chloride produced in the process can also react with the aluminate phases in the cement paste to form chloroaluminate crystals.

$$CaCl_2 + C_3A \rightarrow C_3A{\bullet}CaCl_2{\bullet}10H_2O \quad (1.6)$$

As indicated by Equation 1.6, chloroaluminate forms from the reaction between the chloride solutions and C_3A (Ramchandran et al. 1976, Chatterji 1978, Berntsson & Chandra 1982, Ftikos & Parissakis 1985, Worthington et al.1988, Day 1992, Bonen & Sarkar 1994, Kurdowski et al. 1994, Tumidjski & Chan 1996). This is basically a transformation of the cement hydration product ettringite. The chlorides in solution are thought to cause a replacement reaction in which the sulfate of ettringite is replaced by chloride, with the formation of structurally similar trichloroaluminate (Day 1992). An earlier study by Neville (1969) suggests that the chlorides could solubilize the ettringite and deposit calcium chloroaluminate. However, it could transform back to ettringite by later sulfate ingression. This reaction is related to the chloride concentration, rather than the sodium, and can be observed with interactions with $MgCl_2$ and $CaCl_2$ solutions as well.

It appears that this reaction would be expansive, although there is no mention in the literature regarding the expansive pressures that would be exerted, or whether it would be damaging in and of itself. Marchand et. al. (1994) state this reaction "may significantly reduce the long-term frost durability of concrete surfaces in service." However, the fact that the total amount of chloroaluminates formed is independent of the chloride concentration (Midgley and Illston 1984) but depends instead on the aluminate phase's content (Birnin-Yauri and Glasser 1998) may limit any detrimental effect in concrete.

Buck (1985) mentions that chloroaluminate preferentially replaces ettringite when salt is present. Buck also discusses that chloroaluminate formed during initial hydration in the presence of calcium chloride could later convert to ettringite if the solution becomes rich in sulfate ions. Research conducted by Sutter (2000) has demonstrated the presence of

chloroaluminate in South Dakota pavements. It was commonly found associated with ettringite in air voids and cracks. Figure 1.3 below shows a scanning electron microscope (SEM) micrograph and energy dispersive spectrometry (EDS) analysis of a ettringite/Friedel's salt filled air void from I-94 near Spearfish, SD. This road was badly deteriorated and one of the causes was deicer attack to the cement paste.

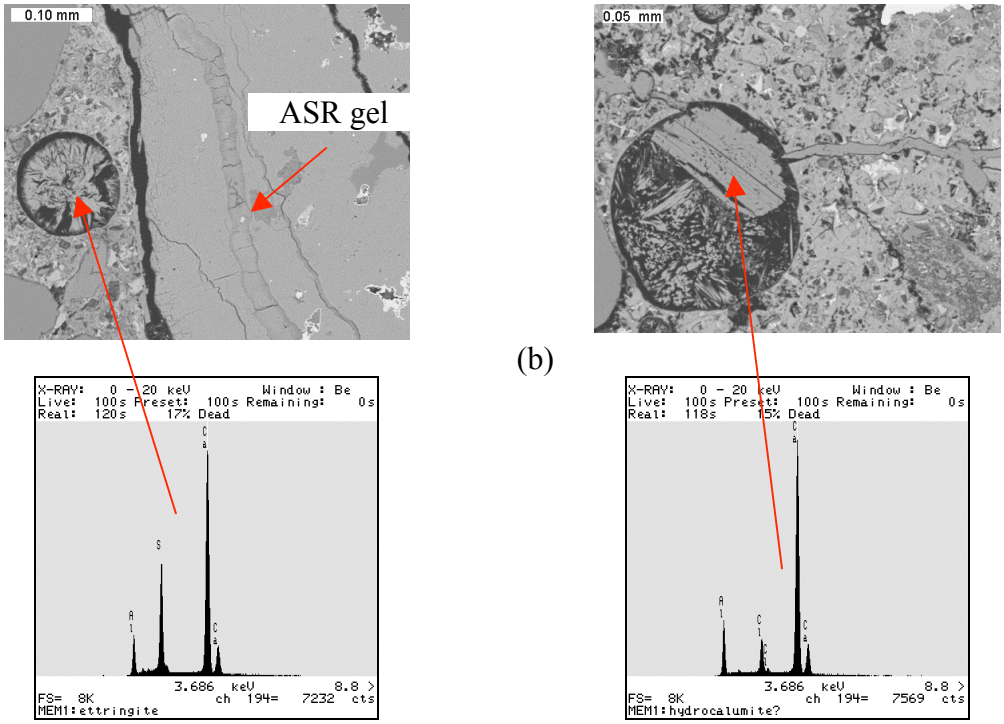

Figure 1.3. Ettringite (a) and hydrocalumite (b) in-filling in void and crack, respectively. Example spectra from each phase are shown in (c) and (d), respectively.

1.2.2.2 Effects of Magnesium Chloride

Like other deicers, $MgCl_2$ effectively reduces the temperature at which water freezes and will have similar physical effects on concrete as NaCl. However, when the $MgCl_2$ occurs in the melt water on the concrete surface, the subsequent chemical interactions that occur may have a negative impact as the solution ultimately penetrates into the concrete. This concern has also been raised in Canada where evidence of $MgCl_2$ having deleterious effect in concrete has been gathered from literature review and presented in transportation association meetings (Hansson and Laurent 2000). Some interactions of magnesium and chloride ions with the cement hydration products in cement paste are known to cause damaging alterations to the cement paste structure, reducing concrete strength while increasing porosity. These changes result from the ability of magnesium and chloride ions to deplete calcium hydroxide to form brucite and calcium chloride. These ions also cause decalcification of the hydration product calcium silicate hydrate, making the paste very porous and converting it to the secondary product, magnesium silicate hydrate. magnesium silicate hydrate is non-cementitious and tends to develop shrinkage cracks, which lead to crumbling of the hydrated cement paste (Lee et al. 1998). Similar compounds are observed after exposing concrete samples to magnesium sulfate, which is a more aggressive solution than magnesium chloride (Frigione and Sersale 1989).

The general reactions for the formation of brucite and magnesium silicate hydrate from $MgCl_2$ are as follows:

Brucite: $Ca(OH)_2 + MgCl2 \rightarrow CaCl2 + Mg(OH)2$ (1.7)

MSH: $CSH + MgCl2 \rightarrow CaCl_2 + MSH$ (1.8)

The reaction Equation 1.8 shows that chloride ions cause calcium to leach from calcium silicate hydrate, producing very soluble $CaCl_2$ and weakening the cement paste structure by increasing its porosity. chloride ions will allow the precipitation of chloroaluminates at early stages of hydration (Moukwa 1990). Another study by Santhanam, et al. (2003), shows that the chlorides enter into reaction with C_3A to produce brucite (Equation 1.7) as well as the chloroaluminate compounds, and they both become incorporated within the calcium silicate hydrate. Other problems associated with the formation of brucite is that as it expands into the paste-fine aggregate interface, it may cause further debonding of the fine aggregate; in addition, a dramatic reduction of the pH of the pore solution from 12.6 to 9.6 is evident when nagnesium ions are available for further precipitation of brucite at the expense of calcium hydroxide (Newton and Sykes 1987). The formation of brucite at the surface tends to create a protective layer that diminishes with time (Taylor and Gollop 1997).

The resulting highly porous cement paste is susceptible to additional magnesium ion penetration, which will convert calcium silicate hydrate to magnesium silicate hydrate (Ftikos & Parissakis 1985). A rapid decrease in strength is due to high porosity at early stages of exposure. In addition, a rapid increase in mass results from the large quantity of brucite formed. From SEM observations, magnesium silicate hydrate generally develops under the brucite layer. Many studies indicate that ultimate failure of concrete is the result of formation of magnesium silicate hydrate from calcium silicate hydrate (Santhanam et. al. 2003, Snow 2001). The identification of magnesium silicate hydrate by other techniques is quite a challenge since it has poor crystallinity and its true structure lies between a gel and a crystalline phase. For instance, X-ray diffraction shows three major broad peaks at 3.6-3.0 Å, 2.6-2.3 Å and 1.6-1.5 Å (Brew and Glasser 2005). In general, magnesium chloride is considered more damaging than sodium chloride due to the instability of calcium hydroxide and the decomposition of calcium silicate hydrate under the chemical attack of magnesium chloride (Helmy et al. 1991). However, it is worth noting that the formation of magnesium compounds are initially limited to the concrete surface layer and the fact that brucite has low solubility may reduce the ability of magnesium ions to penetrate deep into concrete, so carbonation may play an important role in the mechanism of transport (Brown and Doerr 2000).

In addition, Cody and Spry (1994) also reported that both durable and non-durable concrete exposed to $MgCl_2$ were severely deteriorated in their experiment with dolomite aggregates. In the wet/dry cycling, it was seen that the paste and aggregate experienced cracking and precipitation of new mineral, which filled the cracks and other voids. Some laboratory specimens "developed a complex three-layered mineral crack filling" and other stages produced layers of calcite and brucite which were eventually covered by precipitates of "very fine-grained, poorly consolidated minerals containing Fe, Mg, O, Cl, S, and Al" (Cody & Spry 1994). Like other studies, it was reported that the cement paste gained magnesium ions and lost calcium ions through reactions between the aggregates, paste and $MgCl_2$ deicer.

Furthermore, reaction rims were seen in the paste and aggregate after exposure to $MgCl_2$. These rims, when observed with an electron microprobe, showed voids in the dolomite rims filled with brucite and $MgCl_2$; paste rims were depleted of calcium and enriched with magnesium and the voids and pores were filled with $MgCl_2$ precipitates (Cody & Spry 1994).

Other studies have investigated the impact of SCMs on minimizing degradation. The use of GGBFS cement has proven to be beneficial when the level of replacement are kept between 45 to 80% for mortar samples immersed in solutions with 25% $MgCl_2$ by mass compared with replacement outside this range and plain portland cement (Riedel et al. 1967, Smolczyk 1966). In these studies,, no deterioration was observed even after two years of exposure while portland cement samples were destroyed after 6 months (Kleinlogel 1950). One of the reasons for this good performance has been attributed to the lower calcium hydroxide content in the GGBFS blends at the start exposure when compared with portland cement mixes (Tumidajski and Chan 1996) as well as the lower porosity of the paste and lower Ca/Si ratio of calcium silicate hydrate (Ftikos and Parissakis 1995).

Even though less well known, the formation of magnesium oxychloride compounds, namely 3-form ($3Mg(OH)_2 \bullet MgCl_2 \bullet 8H_2O$) and 5-form ($5Mg(OH)_2 \bullet MgCl_2 \bullet 8H_2O$) could be part of the reaction products in concrete samples under the action of concentrated magnesium chloride solutions (Monosi and Collepardi 1993). Both oxychlorides are stable below 212 ºF [100 ºC], being the 5-form more stable than the 3-form when exposed to carbon dioxide (Castellar et al. 1996). These two magnesium oxychloride compounds have been extensively studied under the $MgO\text{-}MgCl_2\text{-}H_2O$ system and are part of the hydrated products of magnesium oxychloride or Sorel's cement (Dehua and Chuanmei 1996). Unfortunately, the resistance of Sorel's cement to continuous moist environment is poor (Li et al. 2003). However, the addition of soluble phosphates such as H_3PO_4, $NaH_2PO_4 \bullet 2H_2O$ and $NH_4H_2PO_4$ has been reported as a way to improve the stability of magnesium oxychlorides compounds when exposed to water (Deng 2003).

Similar to many hydrated basic magnesium salts, these oxychlorides are needle-like crystals, isomorphous and up to 0.1 mm long (Wolff and Walter-Levy 1953, Tooper and Cartz 1966). Characteristic X-ray diffraction peaks are located at 7.491, 4.146 and 2.426 Å for the 5-form and at 8.144, 3.874 and 2.452 Å for the 3-form (Dehua and Chuanmei 1996). The minimum concentration of magnesium chloride needed for the formation of magnesium oxychloride in the $MgO\text{-}MgCl_2\text{-}H_2O$ system has been reported as 1.96 M (Dehua and Chuanmei 1999). It is interesting to add that it is probable that brucite could transform into magnesium oxychloride after exposure to concentrated magnesium chloride solutions of 2 molal and above based on studies of the solubility of both compounds (Altmaier et al. 2003).

1.2.2.3 Effects of Calcium Chloride

Collepardi et al. (1994) cited a number of studies that have concluded that $CaCl_2$, another common deicer, is associated with a deleterious chemical reaction with concrete. The chemical attack is accompanied by the formation of a hydrated calcium oxychloride according to the following reaction:

$$3Ca(OH)_2 + CaCl_2 + 12H_2O \rightarrow 3CaO \bullet CaCl_2 \bullet 15H_2O \qquad (1.9)$$

The reaction proceeds most efficiently at temperatures just above freezing (40 °F to 50 °F [4 ºC to 10 ºC]), with rapid formation of hydrated calcium oxychloride. This reaction is

considered to be disruptive to the concrete matrix because of the hydraulic pressures generated. The destructive nature of the formation of calcium oxychloride could also be explained by the crystal growth pressure theory (Chatterji and Thaulow 1997). Collepardi et al. (1994) speculates that the damaging nature of this reaction has been masked by corrosion of reinforcing steel and freeze-thaw deterioration of the paste and state that the chemical degradation that occurs is very detrimental. Collepardi et al. cites experimental evidence, based on decreasing compressive strength, suggesting that severe deterioration occurred in non-air entrained concrete exposed to $CaCl_2$ deicers even though there was no steel to corrode nor was the concrete subjected to temperatures below freezing.

Collepardi has done other research on the chemical effects of $CaCl_2$ on cement paste using X-ray diffraction techniques. Analysis of degraded cement paste specimens revealed X-ray diffraction profiles characteristic of the hydrate monochloroaluminate ($C_3A•CaCl_2•10H_2O$) and also of the oxychloride $3CaO•CaCl_2•15H_2O$. The X-ray diffraction profiles corresponding to the oxychloride presence were found only in specimens that were analyzed when moist. Similar analyses were performed with dried samples, but failed to reveal the oxychloride diffraction pattern. Calcium oxychloride has been found to be unstable at 68 ºF [20 ºC] and 20% relative humidity, which are normal laboratory conditions (Shi 2001). Therefore, it is believed that previous researchers had not connected $CaCl_2$ paste damage to the oxychloride presence given that the oxychloride presence in dried cement paste is not discernable by X-ray diffraction (Monosi et al. 1990).

On the other hand, the presence of calcium hydroxide seems to be necessary for the formation of calcium oxychloride as per work done in alkali-silica reaction, the exposure of cement paste samples to highly concentrated solutions of $CaCl_2$ (30% by mass) at 104 ºF [40 ºC] can cause calcium hydroxide leaching so that no free calcium hydroxide is available for calcium oxychlorides to form (Chatterji 1979).

The studies cited above used portland cement mixes to prepare test specimens; however, replacement of up to 75% blast-furnace slag has proven to be beneficial against calcium chloride attack as calcium oxychloride could not be found even after 2 years of exposure and the specimens remained in good conditions (Feldman and Ramachandran 1980). Likewise, the use of silica fume modifies the cement paste microstructure by reducing the total porosity, making it more difficult for ions to either penetrate or leach out as shown by experimental data and numerical models (Delagrave et al. 1997).

Other studies have shown another manner in which $CaCl_2$ can potentially affect both aggregates and hydrated cement paste within concrete. Concrete containing reactive dolomite aggregates is susceptible to attack when exposed to $CaCl_2$ solution. This occurs as the $CaCl_2$ solution enhances reactivity in aggregates, releasing magnesium ions, which then form destructive brucite and magnesium silicate hydrate as previously discussed. Alteration rims around the aggregates were observed to contain a considerable amount of calcite prior to $CaCl_2$ exposure, and afterward it appeared that the expansive brucite formation reduced the amount of calcite (Lee et al. 1998). Calcium chloride is reported to also cause concrete deterioration by inducing fracturing immediately adjacent to the coarse aggregate boundaries and oriented parallel to the aggregate-paste interface (Cody et al. 1996). Cody and Spry (1994) found concrete containing reactive dolomite aggregates to be especially susceptible to $CaCl_2$ deterioration. This study focused on dedolomitization, as aforementioned, but also experimented with the effects of $CaCl_2$ deicer on concrete containing dolomite aggregates.

The results, based on EDAX maps, revealed cracks and voids "partially or completely filled with neoformed mineral matter" (Cody & Spry 1994) were rich in $CaCl_2$. Like $MgCl_2$, it was confirmed $CaCl_2$ treatment would also cause dedolomitization. In contrast with the $MgCl_2$ treatments, however, "$CaCl_2$ produced new, highly visible, reaction rims at the margins of coarse aggregates in non-durable concrete under both wet/dry and freeze/thaw conditions" (Cody & Spry 1994).

One unexpected result of their study was the increased content of magnesium in the dolomite rims. A possible explanation is that "with greater $CaCl_2$-induced dedolomitization in he aggregate interior, the aggregate rim will appear magnesium-rich" (Cody & Spry 1994). Although exposure to $CaCl_2$ and $MgCl_2$ will result in deterioration, it is important to keep in mind that texture and porosity play a major role in aggregate, and thus concrete, deterioration.

There are also direct chemical effects of $CaCl_2$ on the cement paste. For example, when exposed to $CaCl_2$ deicer, chloride concentrations tend to increase within the paste causing discoloration. This may be due to the formation of $CaCl_2$ hydrate or to adsorption of chloride ions by calcium silicate hydrate. Iron released from calcium-alumino-ferrite-hydrate also contributes to discoloration (Lee et. al. 1998). Also, significant discoloration of the cement paste has been observed in a previous study by Kosmatka et al. (2002). They attribute these effects to the formation of calcium chloride hydrate phases ($3CaO•CaCl_2•12H_2O$; $CaO•CaCl_2•2H_2O$), to adsorption of Chloride ion by the calcium silicate hydrate phase.

As stated previously, all chloride solutions will cause a transformation of hydration products from ettringite to chloroaluminate. Therefore, in the presence of $CaCl_2$ solutions, pre-existing ettringite will be transformed to calcium chloroaluminate or trichloroaluminate, which has structure similar to ettringite (Day 1992).

Although the amount of chloride bound through the formation of Friedel's salt[2] is higher for samples exposed to $CaCl_2$ than for NaCl, due to the higher pH of the pore solution of the latter (Suryavanshi et al. 1996), the possible competition of calcium oxychloride for hydroxyl ions may allow more Friedel's salt formation in the presence of NaCl than in $CaCl_2$. Once formed, Friedel's salt is more stable at higher alkalinity of the pore solution, so it is expected that the solubility of Friedel's salt will increase with time as carbonation reduces the pH (Suryavanshi and Swamy 1996).

1.2.2.4 Effects of Calcium Magnesium Acetate

Although studies have found that calcium magnesium acetate (CMA) is not as corrosive as NaCl (McCrum 1989), some studies have shown that CMA solutions may be the most deleterious deicing chemical with respect to chemical attack of concrete. Peterson (1995) reported concentrated solutions of CMA dissolved the cement paste in mortar samples during an exposure period of 15 months with the attack being more aggressive at 68 ºF [20 ºC] than at 41 ºF [5 ºC]. Reduction in compressive strength was considerable (up to 23%). The disintegration of the sample was faster in CMA with Ca/Mg ratio of 0.91 compared to CMA solution of 1.26.

[2] Friedel's salt = monochloroaluminate ($CaO•Al_2O_3•CaCl_2•10H_2O$) + trichloroaluminate ($3CaO•Al_2O_3•3CaCl_2•32H_2O$)

A study by Santagata and Collepardi (2000) suggests that CMA causes deterioration of the cement matrix by forming secondary minerals such as magnesium silicate hydrate and brucite. Like $MgCl_2$, CMA solutions transform the cement hydration product calcium silicate hydrate to non-cementitious magnesium silicate hydrate by depleting the calcium. Brucite also forms as a result of CMA penetration into concrete. The magnesium silicate hydrate layer results in shrinkage cracking and debonding of fine aggregate, making the cement more porous. Secondary brucite is then able to precipitate into the large air voids, where ettringite previously existed, created by the loss of fine aggregate. According to Taylor (1990), the dissolution of ettringite occurs due to the decrease in pH caused by the formation of brucite in which magnesium ions consume hydroxyl ions. In addition, calcium ions displaced by the magnesium silicate hydrate forming reaction will precipitate thin layers of calcite on the walls of the air voids and at paste-aggregate interface where brucite also precipitated (Lee et al. 1998). The formation of these secondary minerals results in concrete mass loss, significant decrease in load carrying capacity, and widespread cracking and scaling.

1.2.2.5 Background and Effects of $MgCl_2$ Based Agricultural Products (MBAP)

Magnesium chloride based agricultural products (MBAP) contains agricultural by-products such as silage (condensed solubles from grain processors, brewers, and vinters), whey and steepwater (liquor from processing corn). Developers claim they are "environmentally friendly and non-toxic to vegetation" due to their natural ingredients. It is also stated that another benefit of its natural components is that MBAP tend to inhibit corrosion of concrete caused by chloride salts. Some appealing physical properties of MBAP are that they freeze at lower temperatures than most other deicers, possess a high percentage of deicing solids, and mix readily with liquid chloride brines.

There is a downside, however, to using agricultural by-products in winter maintenance. A study conducted by Roosevelt and Fitch (2000) found that MBAP varies from batch to batch due to the inconsistency of the by-product. As a result of using agricultural by-products, many of the laboratory tests "produced noticeable amounts of mold on the surfaces of the concrete [specimens] where MBAP was used" (Roosevelt and Fitch, 2000). Although, an inhibitor to control mold growth is available, the researchers note that they did not use it for this study.

The main objective of the Roosevelt and Fitch (2000) study was to evaluate the effect of MBAP with other deicers when used as a prewetting liquid. It was found that after 20 freeze-thaw cycles (conducted using conditions specified in ASTM C672 "*Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals"*) concrete blocks subjected to various combinations of MBAP applied alone, with NaCl, and NaCl with $MgCl_2$, that MBAP does not significantly contribute to concrete scaling. In fact, it was found that after the 20 cycles, MBAP applied alone resulted in a 1.13 g cumulative scale weight loss compared to the NaCl applied alone resulted in approximately 260 g weight loss due to scaling.

1.3 Pavement Construction Practices – Effects on Deicer Scaling/Deterioration

1.3.1 Overview

In order to construct durable concrete pavements, it is necessary to approach the mixture design and construction from a holistic point of view. Mehta (1997) presents this concept in a

recent paper. He states that current theories on the mechanisms responsible for deterioration of concrete due to various causes are based on a reductionistic approach to science that tries to understand a complex system by reducing it to parts and then considering only one part of the problem at a time. As a result, current material specifications and test methods are focused only on a series of single attributes, failing to consider the system as a whole. Metha (1997) advocates a holistic approach in which loss of water-tightness is the primary concrete deterioration mechanism, which in turn results in loss of strength and stiffness, and materials-related distress. The two primary mix design considerations for producing deicer scaling/deterioration resistant concrete are proper air entrainment and relatively high cement content with corresponding low *w/c* ratio. These and other factors affecting concrete-deicer interaction are presented below.

1.3.2 Materials

1.3.2.1 Cementitious and Supplementary Cementitious Materials

The selection of cement and SCMs is an extremely important element in designing durable concrete pavements. In many applications, the use of a standard AASHTO M 85 (ASTM C150) Type I cement (described below) will provide satisfactory results. But durability should not be taken for granted, and therefore the properties of the cement and SCMs must be considered in the context of the long-term physical and chemical stability of the concrete pavement.

1.3.2.2 Cement

The standard specification for portland cements used in the United States is presented in AASHTO M 85 (ASTM C150), "*Specification for Portland Cement*". The following cement classifications are presented in the ASTM standard:

Type I—For use when the special properties specified for any other type are not required.

Type IA—Air-entraining cement for the same uses as Type I, where air-entrainment is desired.

Type II—For general use, particularly when moderate sulfate resistance or moderate heat of hydration is desired.

Type IIA—Air-entraining cement for the same uses as Type II, where air-entrainment is desired.

Type III—For use when high early strength is desired.

Type IIIA—Air-entraining cement for the same uses as Type III, where air-entrainment is desired.

Type IV—For use when low heat of hydration is desired.

Type V—For use when sulfate resistance is desired.

The most common cement type employed in pavement construction is Type I. The required chemical properties of Type III cements are similar to Type I, but Type III cements are commonly ground finer to promote the development of higher early strengths. Type III cements are gaining more widespread use, particularly in applications where high early strength is needed such as for rapid setting repairs and "fast track" construction. In areas where sulfate attack is a problem, Type V cements are used. Air-entrained cement,

designated with an "A," have small quantities of air-entraining material inter-ground with the clinker during manufacture.

In addition to these cements, AASHTO M 240 and ASTM C595, "*Specification for Blended Hydraulic Cements*" provides standard specifications for blended hydraulic cements. These specifications recognize the following five classes of blended cements:

Type IS—Portland blast-furnace slag cement

Type IP and Type P—Portland-pozzolan cement

Type I (PM)—Pozzolan modified portland cement

Type S—Slag Cement

Type I (SM)—Slag modified portland cement

These cements are formed by thoroughly blending portland cement with fine materials such as GGBFS, fly ash or other pozzolans, hydrated lime, and pre-blended cement combinations of these materials (PCA 1992). These have not been commonly used on paving projects in the United States, but Type IS, Type IP, and Type I (PM) might be used to produce durable concrete pavements. Each of these three can be further designated as air-entraining (A), moderate sulfate resistant (MS), moderate heat of hydration (MH), or any combination thereof, through the addition of the proper suffix. For example, an air-entraining, moderate sulfate resistant pozzolan modified portland cement would be designated as Type I (PM)-A(MS).

1.3.2.3 Ground Granulated Blast Furnace Slag

Ground granulated blast furnace slag (GGBFS) is a byproduct of the production of pig iron, in which the molten slag (at a temperature of 2700 ºF [1500 ºC]) is rapidly chilled by quenching in water. This forms a glassy, sand-like material that is then finely ground to less than 45 μm, producing a surface area of 400 to 600 m^2/kg Blaine (PCA 1992). GGBFS is nonmetallic, consisting mostly of silicate glass containing calcium, magnesium, aluminum, and silicate with potentially small quantities of crystalline compounds of melilite (Mehta 1993). This rough textured material is cementitious in nature, meaning that it has hydraulic cementing properties on its own. When combined with portland cement, the NaOH or CaOH activates the GGBFS, which hydrates and sets in a manner similar to portland cement (PCA 1992). Specifications for GGBFS for use in concrete are provided in AASHTO M 302 (ASTM C989), "*Specification for Ground Granulated Blast-furnace Slag for use in Concrete and Mortars*".

GGBFS may be blended or inter-ground with the cement and classified according to ASTM C595 as Type IS, Type S, or Type I(SM). Alternatively, it may be added during batching as supplemental cementing materials or as a partial replacement of portland cement.

1.3.2.4 Silica Fume

Silica fume is the byproduct of induction arc furnaces used in the silicon metal and ferrosilicon alloy industries where quartz is reduced to silicon at temperatures up to 3600 ºF [2000 ºC] (Mehta 1993). This produces SiO_2 vapors that oxidize and condense to minute spherical, non-crystalline silica. The particle size is roughly two orders of magnitude smaller than fly ash, having an average diameter of 0.1 μm and a surface area of 20,000 to 25,000 m^2/kg, which is twice that of tobacco smoke (PCA 1992). It is highly pozzolanic, but its

incredibly high surface area makes it difficult to handle, significantly increasing the water demand of the concrete unless water-reducing admixtures are used. Standard specifications for silica fume are provided in ASTM C1240, "*Specification for Silica Fume Used in Cementitious Mixtures*".

Due to its fine size, silica fume is able to pack very tightly into void space between cement and aggregate particles. It can thus be used to significantly reduce concrete permeability, and block the ingress of chlorides. For this reason, silica fume concrete has seen extensive use on bridge decks. Its highly pozzolanic nature also converts alkalis and calcium hydroxide into calcium silicate hydrate making the concrete less susceptible to chemical attack. It can be used to mitigate ASR and sulfate attack (ACI 1992B; PCA 1992), although its effectiveness must be established through testing using ASTM C441, "*Test Method for Effectiveness of Pozzolans or Ground Blast-Furnace Slag in Preventing Excessive Expansion of Concrete Due to Alkali-Silica Reaction*" for ASR and ASTM C1012, "*Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution*" for sulfate resistance.

Silica fume has not been widely used in pavements because of problems encountered in handling and special concerns related to curing. It is also quite costly and is therefore unlikely to find widespread use in pavement applications, except under special circumstances.

1.3.3 Test Methods to Evaluate Concrete Mixture Designs

1.3.3.1 Diagnostic Methods for Identifying Deicer Scaling/Deterioration

Distress related to deicer use is most often associated with surface scaling and delamination, which is almost unique to this distress type. The deterioration is observed in the hardened cement paste, exposing the coarse aggregate particles. This is in contrast to a distress such as "popouts" that is characterized by fractured aggregate particles surrounded by intact paste. If the concrete under evaluation is subjected to deicer applications and is showing signs of scaling, deicers are likely contributing to the distress.

Chemical test methods, such as AASHTO T 260 (ASTM C1152) "*Standard Method of Test for Sampling and Testing Chloride Ion in Concrete and Concrete Raw Materials*" can be used to measure the chloride ion concentration in relation to depth of a concrete specimen. The presence of a high chloride ion concentration at or near the scaling surface is an indicator that the distress is likely related to deicer applications. In AASHTO T 260 pulverized concrete is dissolved in nitric acid to yield dissolved chloride ions in the concrete. Another approach is a water-soluble method ASTM C1218 "*Standard Test Method for Water-Soluble Chloride in Mortar and Concrete*", but it has seen limited use. For the same concrete, the average chloride content measured by the water-soluble method is typically 75 percent to 80 percent of its acid-soluble chloride content (ACI 1989). Chloride content is most often expressed as the chloride ion present as a percentage of the mass of cement. It is very important that the chloride content being reported is defined according to the method of testing.

Determination of deicer deterioration at joint and crack locations is a much more difficult task. The deicer contributes by increasing the level of saturation, increasing the solubility of some compounds, and potentially increasing the alkalinity of the pore water. Thermal shock may also contribute to the occurrence of distress. Under these circumstances, the concrete

becomes more susceptible to other distress mechanisms such as paste and aggregate freeze-thaw deterioration as well as ASR. The deicer may also provide a source of soluble sulfates, resulting in external sulfate attack.

Although the primary distress mechanism may obscure the contribution of the deicer to the deterioration, there are some diagnostic features that are indicators of whether deicer deterioration is at least a contributor to the observed distress. Muethel (1997) examined concrete at crack locations using phenolphthalein to identify calcium hydroxide depletion and permeability measures to estimate coarsening of the paste. He was able to identify zones at the concrete/crack interface that have significantly altered the concrete microstructure compared to the mass concrete, speculating that these differences in microstructure have resulted in joint/crack deterioration and staining. He further states that the primary leaching agent is carbonic acid, which aggressively attacks concrete in a high salinity environment. The presence of chemical deicers thus accelerates the leaching process. Marchand et al. (1994) described a similar process.

It is logical to assume that salts would concentrate in joints or cracks due to infiltrating melt water produced from the deicer application. If the chloride ion concentration were mapped from the joint interface into the concrete mass, the gradient would likely be one in which the concentration would be highest at some distance inward from the joint. The concentration at the interface would be less than the maximum as the flow of water in or through the crack/joint would have a tendency to wash the deicers away while wetting and drying cycles would concentrate them just below the interface surface. Thus, chemical methods could be employed to determine chloride ion concentrations at various distances from the joint/crack face to measure this phenomenon.

One such method for determining the chloride concentration profile is the ASTM C1556, "*Test Method for Determining the Apparent Chloride Diffusion Coefficient of Cementitious Mixtures by Bulk Diffusion*" (Nordtest NTBuild 443). In this test, the sample is first saturated with limewater and then the exposed face of the specimen, similar to specimens used for ponding tests, is exposed to 2.8M NaCl for a minimum of 35 days. Then, the sample is mounted in a mill or lathe and layers of approximately 0.02 inches [0.5 mm] are removed in a direction perpendicular to the surface that was exposed to the salt solution. The dust from each layer is gathered and the chloride content is determined in accordance with AASHTO T 260 (ASTM C1152). From this data a diffusion coefficient and surface chloride ion concentration can be determined (Stanish 2000).

Commonly, a pavement undergoing deicer scaling will have microcracking isolated in, and parallel to, the surface. Polished concrete slabs can be examined to determine at what depth cracking is present. This cracking is very similar to common paste freeze-thaw deterioration (Walker 1992) and in fact the mechanisms are closely related. In addition, if the air-void system parameters in the lower portion of the specimen are adequate, and the paste near the finished surface is devoid of air, poor finishing or curing is likely the responsible mechanism. The same polished slabs can be analyzed using an SEM and EDS system to determine chloride ion concentration profiles or areas of the slab can be analyzed using X-ray mapping to show chloride distribution in the concrete.

A relatively new instrument called an analytical X-ray microscope can also be used to analyze chloride concentration profiles in a polished slab. The analytical X-ray microscope

produces a "focused" X-ray beam by passing the X-ray flux generated from an air-cooled X-ray tube through a fine collimator. The collimators are finely produced glass tubes that taper along their length to a final aperture size of 10 μm, 100 μm, or 300 μm, depending upon the collimator selected by the user. The collimator size determines the point-to-point resolution of the image, or the area of a point analysis performed on the specimen. Using the X-ray microscope in a fluoresced X-ray mode, characteristic x-ray maps can be produced showing elemental distributions and point analyses can be performed to determine the composition of individual phases or individual compositions along a line. The advantage of the analytical X-ray microscope over a SEM is that the analyses do not need to be performed in a vacuum and the relatively large spot size (i.e. 100 - 300 μm) facilitates the measurement of elemental composition less effected by local specimen topography. In the SEM, multiple parallel lines must be averaged to give the same results given the small (i.e. 1-5 μm) analytical spot size resulting from electron beam excitation of the specimen.

Petrography can also be employed to assist in the diagnosis of deicer deterioration. Carefully prepared polished thin sections can be used to identify salt crystals that might be present in addition to ettringite and hydrocalumite. Also, changes in the paste porosity/texture will be identifiable if care is taken in sample preparation. Many researchers have reported that common deicers react with cement paste to form chloroaluminates and oxychlorides, compounds that can be observed through optical petrography and electron microscopy.

Wolter (1997) gives the following characteristics of deicer distress that can be identified using optical microscopy:

- Microcracking propagating around aggregate particles and though the paste only.
- Aggregates relatively intact with virtually no reaction rims of silica gel observed,
- Deterioration within the paste only.
- Microcracking within the paste occurring predominantly sub-parallel to the deteriorating surface.
- Secondary deposits of ettringite within the air-void system and microcracks.
- Less microcracking and secondary deposits as distance increases from the deteriorating surface.

When diagnosing possible deicer distress, the orientation of the sample is important. Ideally, the sample should contain the vertical joint surface, so that the conditions with distance from the joint can be noted. Carbonation, microcracking, and the quantity of ettringite often change dramatically over distances of 1 to 2 in [25 – 50 mm], and samples with unknown orientation to the joint are virtually useless (Wolter 1997).

ASTM C672 "*Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals*" is the most common test used to investigate the scaling potential of concrete. In ASTM C672, a $CaCl_2$ solution (other chemical deicers may be used) is ponded on the surface of rectangular concrete specimens that are then subjected to freeze-thaw cycling. The specimens are placed in a freezer 0 °F (-18 °C) for 16 to 18 h and then manually removed to a thawing environment for 6 to 8 h. A surface layer of the water/salt solution is maintained at all times. A visual inspection is made at 5, 10, 15, 20, 25, and 50 cycles. The concrete is rated on a scale of 0 to 5 (e.g. 0 is for concrete surfaces showing no sign of scaling and 5 is for a surface that is severely scaled with coarse aggregate visible over the

entire surface). The subjectivity inherent in the rating scale is one problem with this test (Pigeon and Plateau 1995). As a result, it is becoming common for researchers to measure the mass of scaled material to gain a more objective measure of scaling resistance.

Concrete made with fly ash and GGBFS have exhibited variable deicer scaling resistance, and therefore mixtures containing these materials should be lab tested if field experience does not exist. Control samples of mixes with known scaling resistance should also be tested, as the results of this test are qualitative.

The Böras method (Swedish Standard SS 13 72 44) is similar to ASTM C672, but has been modified to more accurately represent field conditions. A freezing front passes from the top of the specimen downward. This test allows for testing of specimens obtained from *in situ* structures as well as those prepared in the lab. A rating is assigned based on the mass of scaled material. Although similar to ASTM C672, Pigeon and Plateau (1995) believes that it is a better test for evaluation of scaling resistance. Unfortunately, the correlation between laboratory tests and field performance is not very good (Pigeon 1994; Mehta 1991).

1.3.3.2 Diagnostic Methods for Determining Permeability

It has been shown that concrete subjected to repeated applications of deicers along with wetting and drying cycles develops a coarser pore structure, characterized by larger, interconnected pores. Concrete permeability thus increases, making it more susceptible to many other distresses. This connection has been described by a number of researchers. For example, Basheer (1994) has proposed a single model that links concrete permeability to corrosion of steel, frost damage, chloride ingress, carbonation, sulfate attack, salt attack, alkali attack, acid attack, alkali-aggregate reactions, and abrasion. It therefore may be possible to use the increased permeability associated with deicer deterioration as a diagnostic tool by comparing concrete obtained near joint and crack interfaces to that obtained from a slab interior.

Two widely accepted standard test methods for measuring concrete permeability are the British test method (*British Initial Surface Absorption Test*) that is not commonly used in the United States and AASHTO T 277 (ASTM C1202) "*Standard Method of Test for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration*", or rapid chloride permeability test (RCPT). Many other test methods exist, but none has gained greater acceptance than the RCPT. Strategic Highway Research Program (SHRP) researchers recommended modifications of the AASHTO T 277 (ASTM C1202) test to make it more rapid (Zia et al. 1993). It was also advocated by SHRP researchers that a "pulse pressure" method for concrete permeability be adopted to measure water permeability in the laboratory (Roy et al 1993a; 1993b). A third SHRP test method was proposed for field evaluations in which the rate of airflow through a concrete surface under an applied vacuum is measured to estimate permeability. Unfortunately, this test is not considered sufficiently quantitative for prediction of actual permeability and thus results should only be used as an indicator of permeability (Whiting et al. 1994). More recently, a concrete sorptivity test, ASTM C1585, *"Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes,"* provides an indirect method to assess concrete permeability.

Mobasher and Mitchell (1988) published the results of a large study investigating the applicability of the RCPT. They found that the "test is valid and can be used with confidence." They investigated the repeatability of the test, finding the single operator

coefficient of variation (COV) of a single test result to be 12.3 percent and the multi-laboratory COV to be 18.0 percent. Misra et al. (1994) report that the RCPT can be used as an important tool for quality control, inspection, and design, although further research is needed to examine the effect that pore solution chemistry has on the results. This is a very important finding from the perspective of using this test as a diagnostic tool, as the pore solution in concrete near joints and cracks will be different than that elsewhere due to the ingress of deicing chemicals.

In their investigation of the RCPT, Feldman et al. (1994) reported how changes in experimental conditions and specimens affected results. It was observed that the test affected the pore structure and resistivity of concrete, particularly relatively young concrete. It was also stated that simple measurement of initial current or resistivity gave the same ranking for the four concrete specimens tested, and therefore this might be able to replace the RCPT. It is noted that all the concrete produced had a *w/c* ratio of 0.55, and that their findings need to be verified for lower permeability concrete, and that made with blended cements.

Although the RCPT has been embraced by many SHAs due to its ease of use, it suffers some limitations that make it impractical when evaluating some mixtures. The three main limitations are: 1) the current passed is related to all ions in the pore solution and not just chloride ions, 2) the measurements are made before a steady-state migration is achieved, and 3) the temperature of the specimen increases due to the applied voltage (Stanish et al. 2000). The first limitation is most problematic for the assessment of concrete permeability in mixtures containing various admixtures (e.g., accelerators, corrosion inhibitors, etc.) that will affect the ion concentration of the pore solution.

AASHTO T 277 (ASTM C1202) provides excellent correlation to the results obtained by AASHTO T 259 "*Standard Method of Test for Resistance of Concrete to Chloride Ion Penetration*" for a wide variety of concrete types and qualities (Perenchio 1994). One exception is concrete made with silica fume because the active pozzolanic nature of the material makes it seem more impermeable to chloride ion penetration than it really is. Another exception is concrete made with certain admixtures that affect the electrical conductivity of the mixture, including calcium chloride or calcium nitrite. Regardless, the rapidity, ease of use, and reliability make this test very attractive when investigating not only the chloride ion permeability characteristics of concrete, but also to assess permeability in general. Table 1.3 can be used to make a general assessment of the chloride ion permeability of the concrete tested using this test method AASHTO 277 (ASTM C1202). It is noted that the assessment is not specific, but instead the chloride permeability is assigned a qualitative rating. Pavement concrete should have a qualitative permeability not greater than low, and in aggressive environments (exposure to chemical deicers, sulfates, etc.), a qualitative rating of very low or less is desirable.

Table 1.3. Chloride ion penetrability based on charge passed (AASHTO T 277).

Charge Passed (coulombs)	Chloride Ion Permeability
>4,000	High
2,000-4,000	Moderate
1,000-2,000	Low
100-1,000	Very Low
<100	Negligible

Another approach to understanding the potential susceptibility of concrete to deicer attack is to measure the concrete porosity. Porosity is a measure of the proportion of the total volume of pore space in concrete irrespective of the interconnectivity of the pores (Neville 1996). Absorption tests can be used to measure porosity, but the degree of interconnectivity between the pores influences the measured absorptivity. Thus, although porosity and absorptivity are commonly correlated, there is not a direct relationship. A variety of techniques are used for determining the absorption rate of concrete. One common test is ASTM C642, *Test Method for Density, Absorption, and Voids in Hardened Concrete,* which entails drying a concrete specimen at 212 to 230 ºF [100 to 110 ºC] and then immersing it in water at 70°F [21 ºC] for at least 48 h. This type of test is commonly used as a quality control test for precast members.

As a result of shortcomings in common absorption testing procedures (e.g., ASTM C642), there has been movement toward a type of testing known as sorptivity testing. Sorptivity testing measures the rate of absorption by capillary suction of water into the concrete (Neville 1996). Generally, it is too difficult to mathematically model this flow in all but a single direction, and thus sorptivity tests are configured to establish one directional flow into the specimen (Stanish et al. 2000). Sorptivity tests typically require that the sample be at standard moisture content before starting the test. The benefits of sorptivity testing are reduced time, low cost of equipment, and simplicity of procedure. The new standard, ASTM C1585, "*Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes,"* requires only a scale, a stopwatch, and a shallow pan of water. One attractive feature of this approach is that the sample is conditioned for 7 days, with the temperature never exceeding 122°F [50 ºC]. This is important since damage to the concrete microstructure can result at the higher drying temperatures (212°F [100 ºC] or higher) recommended in other test methods, thus biasing the test results. Data reduction includes plotting the gain in mass per unit area over the density of water versus the square root of elapsed time, with the slope of the best-fit line being the sorptivity.

1.3.4 Construction Considerations for Preventing Deicer Distress

Construction can have a very important impact on the occurrence of materials related distress. As stated, durable concrete must be relatively watertight and non-reactive. From a construction perspective, this means that it must be well mixed, consolidated, and cured under conditions that will produce stable hydration products. Construction practices that have a direct impact on mixing, consolidation, and curing include ambient and seasonal construction conditions, duration of the mixing cycle, method of consolidation, steel placement, finishing, and curing. The following discussion focuses exclusively on those elements of the construction sequence that have a direct bearing on concrete durability.

1.3.4.1 Ambient and Seasonal Construction Conditions

Ambient and seasonal conditions can play an important role in the durability of concrete through their influence on the development of drying shrinkage cracking, excessive heat of hydration, and inadequate curing prior to deicer application. Hot-weather and cold-weather construction practice, as described in *Design and Control of Concrete Mixtures* (PCA 1992) and elsewhere, must be followed. It is imperative that drying shrinkage cracking be avoided to maintain the integrity of the concrete surface. This can only be accomplished if an

awareness of the relationship between relative humidity, temperature, and wind exists and is acted upon by the construction team.

1.3.4.2 Consolidation

The goal of consolidation of paving concrete is the removal of entrapped air while avoiding segregation and disruption to the entrained air system. Assuming that a high quality, well-graded, workable mixture is used, it should be easily consolidated through internal or external vibration, or both. Internal vibration is applied through immersion-type vibrators typically located after the strike-off in the paver. Important factors to consider are the frequency of vibration, amplitude, and the speed of paving. Frequency is typically set between 7,000 and 12,000 vpm, although a recent study recommends fixing the frequency at 10,000 vpm (Gress 1997). This same study recommends weekly calibration checks on the vibrators, a negative (down from horizontal) vibrator slope of 30º or to one-half the pavement depth, and a fixed, uniform paver speed. Other sources state that 8,000 vpm is more typical. In any event, it is critical that the vibration is set to consolidate the concrete without segregation.

It is emphasized that under-vibration can result in poor consolidation and over-vibration may lead to segregation and the disruption of the air void system in the immediate vicinity of the internal vibrator. It has been noted on a number of projects affected by durability problems that the vibrator trails are visible on the pavement surface and appear to be an initiation point for cracking, spalling, and scaling (Gress 1997). In some instances, petrographic analysis has revealed that the air content in the path of vibration is significantly less than that between the vibrators.

When constructing concrete pavements, considerable attention must be directed to produce a mix that has consistent consolidation characteristics. A paving rate and vibrator frequency must be established early in the project that adequately consolidates the concrete without harmful segregation or disruption to the air void system. If the mix is found to be harsh and difficult to place, construction should be stopped until the problem is corrected. Too often, difficulties in placement are not discovered until a pavement begins to suffer early signs of deterioration at which point little can be done.

1.3.4.3 Steel Placement

The placement of embedded steel in concrete pavement has a direct bearing on the potential for corrosion. Steel used at joints, such as dowel and tie bars, is typically placed at mid-depth, thus concrete cover is not an issue. But in these applications, the joint provides a direct route for chloride ion and moisture ingress, and thus these bars must be protected with a durable coating to avoid corrosion. Epoxy is the most commonly used protective coating, although the cladding of dowels with plastic and stainless steel has also been used by some agencies.

For reinforcing steel, adequate concrete cover is essential to prevent corrosion. At least 2 inches [50 mm] of quality concrete cover is required in environments where chloride-based deicers are used. To ensure that at least 90 to 95 percent of the reinforcing steel is adequately protected, it is recommended that a design cover of 2.5 inches [65 mm] be used. Thus, during construction, great care must be exercised to avoid “high steel” which is susceptible to corrosion.

1.3.4.4 Finishing

In slipform paving, mechanical floating is commonly used immediately following the vibrating pan to embed large aggregate particles, correct small surface imperfections, and "close the surface." If the entire slipform paving operation proceeded smoothly, no other finishing other than texturing may be required. But in most cases, additional finishing is needed to correct surface imperfections.

After paving, the surface is checked using a 10 to 13 feet [3 to 4 meter] straight edge. Surface imperfections are commonly corrected using a hand-operated float. It is common that little bleed water occurs with stiff, slip-formed concrete, but under certain conditions, it may be present. It is emphasized that finishing should not be conducted when bleed water is present, as there is a danger that either bleed water will become trapped beneath the concrete surface creating a plane of weakness or air content in the surface layer will be reduced. In either case, scaling of the surface may occur due to freeze-thaw damage, particularly if chemical deicers are used.

Finishers commonly desire to add more water to the surface to assist in the finishing operation. It is known that this demand must be resisted as working water into the concrete surface will increase the *w/c* ratio and reduce the air content, leading to scaling. If the mix is difficult to work without water being added during finishing, the entire construction operation should be reviewed.

On occasion, a paving edge may slump, requiring correction. In this case, it should be carefully rebuilt with added concrete, working against a bulkhead placed against the slab edge. Care must be taken to avoid over-working or over-finishing the repair.

1.3.4.5 Curing

Gowripalan (1993) found that improper curing resulted in the surface having a high rate of evaporation that produced a porous, permeable, and weak surface due to insufficient hydration. He also cited research that found that near the surface, the permeability of poorly cured concrete could be as much as ten times that of well-cured concrete.

Ideally, concrete would be cured in such a way that the presence of mixing water is maintained. This requires the continued application of water either through ponding, fogging, or covering the concrete with a saturated cloth such as burlap. Unfortunately, wet curing is not practical for most large paving projects. Instead, the most common curing method is to prevent the loss of mixing water through the application of a membrane-forming curing compound as specified under AASHTO M 148 (ASTM C309), "*Specification for Liquid Membrane-Forming Compounds for Curing Concrete*". The effectiveness of curing compounds can be assessed through AASHTO M 155 (ASTM C156), "*Test Method for Water Retention by Liquid Membrane-Forming Curing Compounds for Concrete*".

The curing compound should be applied immediately following texturing. Any delay, particularly during hot, windy conditions, can cause significant harm to the concrete resulting in plastic shrinkage cracking. Although these cracks are small and isolated to the concrete surface, they provide access for deicing solutions into the concrete structure.

Great care should be exercised in the application of curing compounds. The application must be uniform and of sufficient quantity to ensure that the surface is completely sealed. On large

paving projects, power-driven spray equipment should be used. It is highly recommended that two coats be applied to ensure complete coverage (PCA 1992).

There are concerns that some curing compounds are not effective. Highway agencies are highly encouraged to test curing compounds to verify their moisture-retention properties. Water-based curing compounds should not be "watered down" during construction. Also, the curing compound should be resistant to damage caused by construction traffic.

Different concrete mixtures will require different lengths of curing prior to opening to traffic. This must be carefully considered when concrete mixtures containing fly ash or GGBFS are used. Temperature also has a major effect on the required length of curing, and the use of maturity concepts to determine appropriate opening times is recommended. In addition to strength gain required for load carrying capacity, newly placed concrete also requires an air-drying period of 1 month before it is subjected to deicer applications. This will add to the scaling resistance of the concrete.

1.3.5 Preventive Strategies for Controlling Specific Types of Materials-Related Distress

1.3.5.1 Deicer Scaling/Deterioration

In general, deicer scaling is not a concern for properly constructed, high quality portland cement concrete. But even if the concrete is properly constructed and cured, deicers may damage concrete with poor mix characteristics. Pigeon (1994) comments on this by stating, that "air entrainment improves to a very large degree the resistance to deicer salt scaling…and as could be expected, scaling decreases with water-cement ratio, and finishing and curing operations are particularly important." As indicated, the two primary mix design considerations for producing deicer scaling/deterioration resistant concrete are proper air entrainment and relatively high cement content with corresponding low *w/c* ratio.

Air content is an important consideration when trying to prevent deicer scaling. Concrete, adequately air-entrained for freeze-thaw, may be susceptible to the development of salt scaling. Collepardi et al. (1994) concludes that air contents recommended by ACI for "severe exposure" should be followed if the concrete is to be exposed to calcium chloride deicers, finding that concrete with air contents meeting ACI "moderate exposure" requirements suffered severe degradation in laboratory testing even without being subjected to freeze-thaw action. The ACI recommendations are presented in Table 1.4 (ACI 1992).

In addition to the use of entrained air, high cement content, and low *w/c* ratio, the use of fly ash has been proposed to enhance deicer scaling/deterioration resistance. The PCA (1992) reports that air-entrained concrete containing fly ash has similar freeze-thaw durability to concrete made with portland cement as the sole binder as long as the same compressive strength, air void system, and curing are obtained. The results of a study conducted by Malhotra (1991) agree with those by Malek (1988) in which it was found that the incorporation of fly ash (two ASTM Type F and one Type C) appreciably reduced the permeability of concrete to chloride ions. This study was based on measuring chloride ion permeability using AASHTO T 277 (ASTM C1202) and not on a measure of scaling resistance. Bilodeau (1991) found that concrete containing up to 30 percent ASTM Type F fly ash generally performed well under the combined effect of freezing and thawing in the presence of salt deicer, although performance of the fly ash concrete was more variable. Although extended periods of moist-curing or drying periods did not seem to significantly

affect performance, the use of membrane curing had a decided benefit, particularly for fly ash concrete. In a paper published a year later, Bilodeau (1992) reported on the properties of concrete containing ASTM Type F fly ash as 58 percent of the total cementitious materials content. He noted that in addition to acceptable mechanical properties, high volume fly ash concrete had excellent resistance to chloride ion penetration as compared to plain concrete mixes. He mentioned that further testing is needed to demonstrate scaling resistance.

An experiment conducted by Byfors (1987) examined the influence of fly ash and silica fume addition on chloride ion penetration and pore solution alkalinity. It is reported that the additions of either fly ash or silica fume considerably reduces the rate of chloride ion diffusion. Malhotra (1991) cites a number of studies conducted by the Canadian Center for Mineral and Energy Technology (CANMET) that indicate the incorporation of low calcium fly ash (ASTM Type F) in concrete significantly reduces chloride ion penetration.

Table 1.4. Recommended air contents for freeze-thaw distress resistant concrete (ACI 1992).

Nominal Maximum Aggregate Size, inches [mm]	Average Air Content, Percent[1]	
	Moderate Exposure[2]	Severe Exposure[3]
3/8 [9.5]	6	7.5
1/2 [12.5]	5.5	7
3/4 [19]	5	6
1 [25]	5	6
1-1/2 [37.5]	4.5[4]	5.5[4]
3 [75]	3.5[4]	4.5[4]
6 [150]	3	4

[1] A reasonable tolerance for air content in field construction is ± 1.5 percent.

[2] Outdoor exposure in a cold climate where the concrete will be only occasionally exposed to moisture prior to freezing, and where no deicing salts will be used. Examples are certain exterior walls, beams, girders, and slabs not in direct contact with soil.

[3] Outdoor exposure in a cold climate where the concrete may be in almost continuous contact with moisture prior to freezing, or where deicing salts are used. Examples are pavements, bridge decks, sidewalks, and water tanks.

[4] These air contents apply to the whole as for the preceding aggregate sizes. When testing these concretes, however, aggregate larger than 1-1/2 inches [37.5 mm] is removed by handpicking or sieving and the air content is determined on the minus 1-1/2 inches [37.5 mm] fraction of the mixture. (The field tolerance applies to this value.) For this the air content of the whole mixture is computed.

In a large laboratory study, Gebler (1986a) and Klieger (1987) examined the durability of concrete made with both ASTM Type C and Type F fly ash. Both the chloride ion penetration and deicer scaling resistance were measured. It was concluded that fly ash concrete was just as resistant to chloride ion penetration as conventional concrete with similar *w/c* ratio. But it was also found that conventional concrete was more scaling resistant than fly ash concrete, regardless of the type of fly ash used.

Marchand (1994), in a review of salt deicer scaling, reports that many studies are contradictory concerning the scaling resistance of fly ash concrete. He found that many laboratory studies indicate poor scaling resistance of fly ash concrete, yet field studies show adequate performance. He attributes most of these differences to the variable nature of fly ash and to its slow rate of hydration. He concludes that the maximum recommended amount of fly ash should be limited to 30 percent of the total mass of cementitious material.

Detwiler (1994) found that either a 5 percent addition of silica fume or 30 percent addition of slag led to a far greater reduction in chloride ion penetration than did reducing the *w/c* ratio from 0.5 to 0.4. She also noted that increasing the curing temperature over a range from 75 ºF to 160 ºF [23 ºC to 70 ºC] creates large differences in performance that indicates "the importance of controlling the curing process if durability is to be achieved." Her findings seem inconsistent with those of Stark (1997), but this may be explained by Malhotra's findings in which concrete containing fly ash actually has lower chloride permeability but still had poor scaling resistance (Malhotra 1991). Obviously, more research needs to be conducted to determine if fly ash or GGBFS can be used to improve scaling resistance.

1.3.5.2 Corrosion of Embedded Steel

Chapter 3 in ACI 222R (1989) provides an excellent description of how to protect new concrete construction against corrosion. The following three general categories of protection are considered:

- The use of design and construction practices that maximize the protection afforded by the concrete.
- The use of treatments that penetrate or are applied to the concrete surface that prevent chloride ion penetration.
- The use of techniques that directly protect the reinforcement from corrosion.

For pavement construction, the first and last categories are of most practical merit for prevention of corrosion of embedded steel, as the use of protective coatings on load transfer devices and adequate cover over reinforcing steel should be all that is required if properly constructed, high quality concrete is used.

The most effective pavement design factor for resisting corrosion is to provide adequate concrete cover over the embedded steel. In high quality concrete, the carbonation zone is unlikely to exceed 1 inch [25 mm] and thus a concrete cover of 1 to 1.5 inches [25 to 37.5 mm] is considered adequate for many structures (Mindess and Young 1981). But tests have shown that structures subjected to severe chloride exposure should have a concrete cover of at least 2 inches [50 mm] (Mindess and Young 1981; ACI 1992b; Mehta 1993). Thus, reinforced concrete pavements constructed in areas exposed to chloride-based deicers should use a minimum 2 inch [50 mm] concrete cover. It is noted in ACI 201.2R (1992b) that to achieve the desired 2 inch [50 mm] cover in paving for 90 percent to 95 percent of the reinforcing steel, the specified cover should be 2.5 inches [65 mm].

It is important that a high chloride ion concentration not be introduced into the concrete through the constituent materials. One potential source of chloride ions in the constituent materials is the aggregate. In one study cited in ACI 201.2R (1992b), quarried stone, gravel, and natural sands were found to contain chlorides of sufficient quantity that the chloride ion concentration in the concrete exceeded permissible levels. It is noted that chlorides in aggregate are not always available to the corrosion process. Thus, if concrete made with marginal aggregate has had good field performance, higher chloride levels may be tolerated. Calcium chloride accelerator is another internal source of chloride ions and its use should be discouraged if embedded steel is used. The chloride ion concentration of mixing water should also be limited.

Calcium nitrite has been found to be an effective corrosion inhibitor as well as an accelerator (ACI 1992). The nitrite ion chemically interacts with ferric oxides, making them insoluble. This reinforces the passive film, preventing the ingress of chloride ions up to a certain threshold level (PCA 1992). The cost of a corrosion inhibitor can be rather high, adding 8 percent to the cost of concrete (Mehta 1997).

The determination of the chloride ion concentration may be desired since it is an important factor in the corrosion of embedded steel. Chloride ion concentration can be determined using either of two wet chemical analyses. One is used to determine water-soluble chloride whereas the second determines the acid-soluble chloride content. In each case, a concrete specimen is ground to powder, typically using a rotary hammer to avoid the use of cooling fluids. The most common test is the acid solubility test AASHTO T 260 (ASTM C1152), in which the pulverized concrete is dissolved in nitric acid. The water-soluble method (ASTM C1218) has seen limited use. For the same concrete, the average chloride content measured by the water soluble method is typically 75 percent to 80 percent of its acid-soluble chloride content (ACI 1989). Chloride content is most often expressed as the chloride ion (Cl^-) present as a percent of the mass of cement. It is very important that the chloride content being reported is defined according to the method of testing.

The permeability of the concrete to chloride ion penetration can be measured in the laboratory. AASHTO T 259, *"Resistance of Concrete to Chloride Ion Penetration"* was a commonly used test method in which concrete prisms are subjected to ponding of a 3 percent sodium chloride solution for 90 days. The chloride ion concentration is then measured at various depths to assess the degree of ingress.

Due to the long testing period, a rapid test was devised based on the electrical conductivity of the concrete. This test is designated as either AASHTO T 277, *"Rapid Determination of the Chloride Permeability of Concrete"* or ASTM C1202, *"Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration"*. As discussed previously, it has excellent correlation to the results obtained by AASHTO T 259 for a wide variety of concrete types and qualities (except for concrete made with silica fume) (Perenchio 1994). The rapidity, ease of use, and reliability make this test very attractive when investigating the chloride ion permeability characteristics of concrete. Table 1.3 can be used to make a general assessment of the chloride ion permeability of the concrete tested using this test method (ASTM C1202). Because of its usefulness, it is recommended that this test be routinely conducted during mix design as an overall assessment of concrete permeability.

Studies cited in ACI 201.2R (1992b) have shown that for similar cover, the level of corrosion successively decreases with decreasing *w/c* ratio. For concrete exposed to very severe chloride environments, it is recommended that a *w/c* ratio of less than 0.40 be used if possible. In lieu of this, increasing the concrete cover to 4 inches [100 mm] is recommended for cast in place construction in a marine environment having a *w/c* ratio of 0.45. Even the most impermeable concrete can become permeable if cracking occurs. These cracks provide easy access, concentrating chlorides, water, and oxygen to form a cell that can initiate corrosion (ACI 1992b).

Torri (1992) studied the effect of SCMs and environmental conditioning on the concrete pore structure and chloride ion permeability. It was concluded that although the pore structure at the surface of concrete containing mineral admixtures was adversely affected by long-term

drying, that in all cases, mixtures prepared with admixtures had lower chloride ion permeability that comparable mixtures made of ordinary portland cement.

One interesting study concluded that aggregate can be as much as 1000 times more permeable than a high quality portland cement paste and thus an overabundance of aggregate may adversely affect the ability of the concrete to protect steel (Perenchio 1994). It is therefore suggested that the maximum aggregate size and aggregate permeability are important considerations when designing against corrosion. Perenchio states that the use of large coarse aggregate particles may in effect "short-circuit" the concrete cover by providing a more direct route for harmful agents to permeate into the concrete. This should be studied in detail before adopting new gradation requirements.

Even the most impermeable concrete can become permeable if cracking occurs. Thus sound design practices should be used to minimize cracking and to keep cracks that form in reinforced pavements tight, minimizing the infiltration of deleterious agents. Construction practices should be used that prevent plastic shrinkage cracking of the pavement surface through the application of an approved curing compound at the appropriate time. This is most important during dry, windy days when the evaporation of bleed water can be quite rapid. Poor concrete consolidation must also be avoided through the design of a workable mix and care in selecting the appropriate depth, spacing, and operating frequency for internal vibrators.

In rare cases, it may be determined that an existing concrete pavement is at risk of suffering widespread corrosion before active corrosion has actually taken place. For example, a pachometer survey conducted soon after construction may reveal that the steel was improperly placed and adequate cover does not exist. In such a case, an agency may want to take preemptive measures to prevent the future occurrence of corrosion. Various concrete coatings and sealers are available that will prevent or slow down the penetration of water and salts. Silanes in particular have been found to be very effective.

Concrete cover cannot protect dowels and tie bars because the opening at the joint interface allows for the inflow of chlorides, moisture, and oxygen. It is therefore common practice to protect dowels and tie bars from corrosion by using a protective barrier coating such as fusion bonded epoxy. The long-term effectiveness of epoxy coating of embedded steel is currently under intense study (Mehta 1993) although many cite it as an excellent preventive measure (Perenchio 1994). Some agencies have investigated the use of plastic and stainless steel cladding as an alternative coating for dowel bars.

1.4 State-of-the Practice Construction of Concrete Pavements

It is clear from the previous discussion that material selection, mixture proportioning, and construction practices can have a profound effect on the durability of concrete. The need to carefully select materials, properly proportion them, and exercise care in construction is essential when the concrete is to be exposed to a freeze-thaw environment in the presence of deicers. Obvious considerations include the need to select durable aggregates, acceptable portland cement and SCMs, and suitable admixtures, and proportion them to create a dense, relatively impermeable concrete that is not susceptible to physical or chemical attack. Excellent information regarding material selection and proportioning to avoid physical and chemical attack is provided in *Design and Control of Concrete Mixtures* (Kosmatka et. al.

2003) and *Guidelines for Detection, Analysis, and Treatment of Materials-Related Distress in Concrete Pavements* (Van Dam et. al. 2002).

From the perspective of the state-of-the-practice, concrete mix design characteristics are particularly important for creating deicer deterioration resistant concrete include low *w/c* ratio and air entrainment (Pigeon 1994). A high *w/c* ratio produces a weak and permeable hydrated cement paste by increasing the capillary porosity. It is therefore recommended that a maximum *w/c* ratio of 0.45 be used to reduce deicer deterioration (ACPA 1992, ACI 1992, Cody 1994). The use of an air entraining agent creates the finely dispersed air voids in the hydrated paste that are needed to accommodate the pressures that develop as the concrete freezes and thaws.

It is also a commonly held dictum that a minimum cement content of 564 lbs/yd^3 [335 kg/m^3] is needed to increase the scaling resistance of concrete (Kosmatka et. al. 2003). When using ASTM C672 to evaluate the concrete, Ghafoori (1997) recommended using a minimum cement content of 600 lb/yd^3 [356 kg/m^3]. Although the need for minimum cement content is a common feature of many specifications, this approach has been questioned, with some sources stating that it is more critical to minimize the *w/c* ratio while using an aggregate gradation that reduces the cement content (TRB 1999).

One major consideration faced by SHAs when selecting cementitious materials is that portland cements blended with SCM (e.g. pozzolans, GGBFS) often require a longer curing time prior to deicer application to prevent scaling. This is due to the slower rate of hydration inherent in many SCM and the decreased permeability characteristic of such concretes, resulting in a longer drying time. Therefore late season paving with concrete containing SCMs is potentially problematic

It is also widely recognized that concrete subjected to a freeze-thaw environment in the presence of deicing chemicals must be air entrained (PCA; ACI 1992; Van Dam et. al. 2002). Barothel-Bouny (2002) reviewed resistance to deicing-salt scaling in terms of different admixtures (such as air-entrainment admixtures), and the performance of those particular concrete pavements. High performance concretes (HPC) that are not air-entrained performed poorly in the deicing scaling test. The general conclusion of this study, with respect to scaling resistance due to deicing, is that air entrainment has a generally positive effect with respect to scaling resistance.

Air content of concrete was also the primary concern of Collepardi et al. (1994). This research looked at the chemical, rather than physical effects, of chemical deicers on concrete structures. Non-air-entrained concrete had increased chemical action as the *w/c* ratio decreased, and experienced a significant decrease in durability. The durability performance of air-entrained concretes was considerably better than non-entrained concretes. Their recommendation was to use the ACI "severe exposure" recommendations to prevent attack against $CaCl_2$ and freeze-thaw action.

The most critical elements of construction that have an impact on the freeze-thaw durability of concrete subjected to deicers are those that affect the *w/c* ratio or the air-void system. Any aspect of construction that raises the *w/c* ratio can negatively impact durability. Thus the moisture content of the aggregates must be accurately accounted for, the cement must be properly proportioned, and additional mix water must not be added if it will compromise the maximum specified *w/c* ratio. Further, water should not be added or "broadcast" onto the

concrete during finishing, as this will result in a high *w/c* ratio at the surface producing a weak and porous layer susceptible to scaling. Trapping of bleed water by premature floating of the surface can also create a weakened layer of concrete that will be susceptible to scaling.

To ensure adequacy of the entrained air-void system, the air entraining agent must be added at the rate and timing needed to create not only an acceptable air content, but also an air-void system meeting minimum spacing factor and specific surface requirements (ASTM C457, "*Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete*"). Thus standard methods that measure air content may need to be supplemented with methods that measure the actual air-void system parameters such as the air void analyzer (AVA) or ASTM C457. During placement and finishing, the concrete must not be overworked resulting in the loss of entrained air.

Once placed, the best curing regime possible should be used to facilitate hydration of the concrete surface. Ideally wet curing would be utilized, but this is rarely done on paving concrete. If a curing compound is used, the coverage should be thorough to minimize loss of moisture from the surface. And finally, an adequate curing and drying time must be allowed prior to the first application of deicing chemicals.

Table 1.5 presents three key mixture design parameters (*w/c* ratio, cement factor, and air content) obtained from the standard specifications for 31 SHAs that routinely use deicing chemicals. As can be seen, there is considerable variability among the SHAs in specifying these three parameters.

Regarding the *w/c* ratio, when specified (and often it is not specifically defined), it ranges from 0.40 to 0.559, with an average value of 0.467. Based on ACI 318, concrete elements exposed to freezing and thawing in a moist condition in the presence of deicing chemicals should have a maximum *w/c* of 0.45. Although a number of SHAs meet this requirement, a significant number do not. Many of the SHAs that have the higher specified maximum *w/c* ratios are located in regions without notoriously cold winters (e.g. North Carolina, Kentucky, etc.), yet others (e.g. Ohio) are located in regions with frequent freeze-thaw cycles and moderately cold temperatures.

The minimum specified cement content also varies widely. Many SHAs have adhered to the PCA recommendations of using a minimum cement content of 564 lbs/yd^3 [335 kg/m^3] (6 sacks per cubic yard) to prevent scaling. Others have significantly lower minimum values. The air content ranges again vary, but all SHAs reviewed required the use of an air-entraining admixture. Often, SHAs stipulated different air content ranges for different size aggregates, complying with ACI 201 recommendations. New Mexico even stipulated that ASTM C457 air-void system parameters be met.

Not listed in Table 1.5 is that almost all SHA standard specifications allowed for the use of SCMs, often stipulating a maximum allowable amount of fly ash or GGBFS. Some specifications (e.g. Michigan) recognize that additional curing time is needed for mixtures containing SCMs and therefore have seasonal placement limitations. Illinois required the use of a "protective coating" for all concrete pavement placed after a certain date that will be opened to traffic during the winter months. Finishing and curing requirements were consistent with the state-of-the-practice described previously.

Table 1.5. Concrete mixture parameters obtained from SHA standard specifications.

State DOT	*w/c* ratio	Cement Content (lbs/yd^3)	Air Content (percent)
Arkansas	0.45	564	4.0 to 8.0
California	NS	506	4.0
Colorado	NS	656	4.0 to 8.0
Connecticut	0.49	615	4.5 to 7.5
Delaware	0.45	564	4.0 to 7.0
Idaho	NS	560	4.0 to 7.0
Illinois	NS	564	5.0 to 8.0
Indiana	0.45	440	5.7 to 8.9
Iowa	0.43 to 0.488	Varies w/ aggregate	5.0 to 7.5
Kentucky	0.49	564	4.0 to 8.0
Maryland	0.50	580	5.0 to 8.0
Massachusetts	NS	Varies w/ aggregate	6.0 to 8.0
Michigan	NS	564	5.0 to 8.0
Minnesota	NS	Varies w/ aggregate	5.0 to 8.0
Montana	NS	564	4.0 to 7.0
Nebraska	0.42	Varies w/ aggregate	5.0 to 7.5
New Mexico	NS	NS	6.5 to 9.0
New York	0.44	605	5.0 to 8.0
North Carolina	0.559	526	4.5 to 5.5
North Dakota	0.47	564	5.0 to 8.0
Ohio	0.50	600	4.0 to 8.0
Oklahoma	0.48	564	5.0 to 8.0
Oregon	0.48	570	Varies w/ aggregate
Pennsylvania	0.47	587.5	3.5 to 8.0
South Carolina	0.44 to 0.47	588	3.0 to 6.0
South Dakota	0.45	585	5.0 to 7.5
Texas	0.45	NS	Varies w/ aggregate
Utah	0.44	611	5.0 to 7.5
Virginia	0.49	564	4.0 to 8.0
West Virginia	0.49	564	4.5 to 9.5
Wisconsin	0.40 to 0.47	530	5.5 to 8.5

NS: Not specified.

1.5 Literature Review Summary

Traditionally, winter maintenance entails plowing snow and applying chemicals and abrasives to melt the snow and ice cover. Over the years, traditional snow and ice removal methods have been modified in order to comply with environmental regulations, reduce corrosive damage to vehicles, and provide a more economical method to maintain safe roads. Current methods of snow and ice removal include deicing, pre-wetting salt or abrasive material, and anti-icing.

Concrete consists of coarse aggregate, fine aggregate (i.e. sand), portland cement, water, and typically, entrained air. The water and portland cement react to form hydration products, most notably calcium silicate hydrate and calcium hydroxide.

A number of concrete properties affect performance when the concrete is exposed to deicers. The most important characteristics to control are: permeability; air content; cement chemistry; aggregate properties; and cracking.

It is widely understood that the water to cement ratio (*w/c)* has the largest influence on the durability of concrete. By having a relatively low *w/c* ratio, the porosity of the hydration products will decrease and in turn, the concrete will be less permeable.

One important aspect of concrete permeability regarding the application of deicing chemicals is chloride diffusion. The movement of chloride ions in concrete is a function of several variables. These include the concentration of deicer solution at the concrete surface, pore size and spacing, pore volume fraction, changes in pore size with respect to location within the cement paste, and chemical composition of phases present in the hydrated cement paste.

Cracking in concrete significantly increases the permeability and makes the concrete more susceptible to ingress of fluids. Although cracking may not cause immediate structural failure, it may provide for the onset of deterioration that ultimately leads to failure. As cracking spreads, it increases the permeability of concrete, leading to surface scaling and further internal stress-related cracking.

Entrained air has been found to improve the freeze-thaw (F-T) resistance of concrete. It is also known that a disadvantage of increasing the entrained air content is that it lowers the strength and increases the permeability of concrete. However, to have good F-T protection, air entrainment is required.

Both physical and chemical interactions occur within concrete when it is exposed to freeze-thaw conditions and deicing chemicals. Physical interaction is initiated when the saturated concrete freezes, subjecting the concrete to expansion and internal stresses. Additionally, some researchers have reported that the crystallization of salts or other phases within the concrete pore system can also lead to expansive cracking. Chemical interaction results from the interaction of deicing chemicals with the hardened cement paste, leading to possible degradation of the concrete structure. Combined, physical and chemical interactions may lead to distress in concrete pavements.

Deicer scaling/deterioration is typically characterized by scaling or crazing of the slab surface due to the repeated application of deicing chemicals. Although the exact causes of deicer scaling are not known, it is commonly thought to be primarily a form of physical attack, possibly resulting from a combination of factors. Some researchers have stated that

the presence of deicing chemicals can magnify or amplify the mechanisms that lead to F-T deterioration of the paste.

Although most research suggests that physical deterioration is the dominant source of distress associated with deicers, some researchers feel strongly that chemical interactions may also be occurring. It is known that the calcium hydroxide dissolution process results in increased porosity at exposed surfaces, increasing the permeability of the concrete, and the dissolved calcium hydroxide reacts with deicers to form deleterious compounds.

Magnesium chloride ($MgCl_2$) effectively reduces the temperature at which water freezes and will have similar physical effects on concrete as NaCl. However, when the $MgCl_2$ occurs in the melt water on the concrete surface, the subsequent chemical interactions that occur may have a negative impact as the solution ultimately penetrates into the concrete. Some interactions of magnesium and chloride ions with the cement hydration products are known to cause damaging alterations to the cement paste structure, reducing concrete strength while increasing porosity. Magnesium oxychloride compounds can occur as reaction products in concrete samples exposed to concentrated chloride solutions

Other researchers have concluded that calcium chloride ($CaCl_2$), another common deicer, is associated with a deleterious chemical reaction with concrete where calcium oxychloride forms, causing cracks as it expands.

Magnesium based agricultural product (MBAP) deicers contain agricultural by-products in addition to $MgCl_2$. Some appealing physical properties of MBAP deicers are that they freeze at lower temperatures than most other deicers, they possess a high percentage of deicing solids, and mix readily with liquid chloride brines.

One reported way to mitigate problems with deicing chemicals is the partial replacement of portland cement in the concrete mixture with another cementitious material such as fly ash, silica fume, or GGBFS. The use of these industrial by-products has many benefits, including their influence on the heat of hydration and strength. More importantly, they aid in the resistance of concrete to chemical attack by improving the chemical nature and microstructure of the hydrated cement paste by decreasing the amount of calcium hydroxide present and decreasing permeability.

In general, physical attack associated with deicing chemicals is not a concern for properly constructed, high quality portland cement concrete. But even if the concrete is properly constructed and cured, deicers may damage concrete with poor mixture characteristics. The two primary mixture design considerations for producing deicer scaling resistant concrete are a relatively low *w/c* ratio (with corresponding high cement content) and air entrainment. State highway agencies standard specifications reflect this, although the specified maximum *w/c* ratio and minimum cement content vary greatly from state to state, indicating that consensus does not exist among the various agencies. It is not clear if chemical attack can be prevented through sound construction practices alone.

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